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Annotated bibliography of α -benzildioxime

Charles V. Banks

Iowa State College

Michael J. Maximovich

Iowa State College

Nelson J. Fowlkes

Iowa State College

Peter A. Beak

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Abstract

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Disciplines

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 α -Benzildioxime

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Charles V. Banks, Michael J.
Maximovich, Nelson J. Fowlkes,
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AMES LABORATORY
RESEARCH AND DEVELOPMENT REPORT
U.S.A.E.C.



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UNITED STATES ATOMIC ENERGY COMMISSION
RESEARCH AND DEVELOPMENT REPORT

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June 1958

Ames Laboratory
at
Iowa State College
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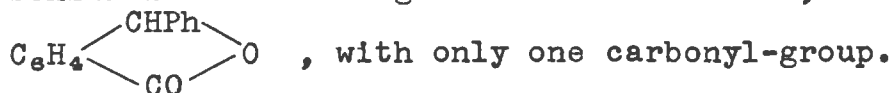
Introduction

The references are presented chronologically. The names and configurations used by each author are retained. In this regard it should be noted that the presently accepted configuration of α -benzildioxime (anti) was not proposed until 1921, and was not generally accepted until somewhat later. The syn-configuration was generally used before 1921.

1883

1. Wittenberg, M., and Meyer, V., "Benzil," Ber., 16, 500
(1883) [J. Chem. Soc. (London), 44, 803 (1883)]

The configuration of benzil is usually expressed as Ph.CO.CO.Ph. The authors have investigated benzil with heated lead oxide and placed its formula in close relationship with benzophenone. With hydroxylamine only one carbonyl-group reacted. It was concluded that benzil had the configuration of a lactone,



2. Goldschmidt, H., and Meyer, V., "Benzil," Ber., 16, 1616
(1883) [J. Chem. Soc. (London), 44, 1120 (1883)]

It was found that Wittenberg and Meyer's compound (Ber., 16, 500 (1883)) forms a glyoxime (m.p. 237°) when treated with hydroxylamine and hydrochloric acid in methanol. The new compound, diphenylglyoxime, is soluble in alcohol and ether. Strong alkaline solutions dissolve it, and the alkaline derivative forms a yellow precipitate with silver nitrate.

3. Goldschmidt, H., "Action of Hydroxylamine on Diketones," Ber., 16, 2176 (1883) [J. Chem. Soc. (London), 46, 62 (1884)]

An isomer of diphenylglyoxime was prepared and isolated. The new isomer was named β -diphenylglyoxime. It differs from the α -isomer in its melting point (206°), appearance, and greater solubility in water and alcohol. The α -isomer (m.p. 237°) is converted to the β -form when heated to 180°.

1886

4. Koreff, R., "Derivatives of β -Naphthaquinone," Ber., 19, 176 (1886) [J. Chem. Soc. (London), 50, 363 (1886)]

Research was done on naphthaquinonedioxime. The author gave the following formula, $\begin{array}{c} \text{CPh:NO} \\ \diagdown \quad \diagup \\ \text{CPh:NO} \end{array}$, to the oxidized product of diphenylglyoxime which is similar to the oxidized product of naphthaquinonedioxime. Oxidation was done with ferricyanide in basic solution.

1887

5. Beckmann, E., "Isonitroso-compounds," Ber., 20, 1507 (1887) [J. Chem. Soc. (London), 52, 826 (1887)]

An intramolecular change is noticed when diphenylketoxime is treated with phosphorus pentachloride or strong sulfuric acid. The product precipitates from water and gives benzonitrile upon addition of sodium carbonate.

A similar reaction product (m.p. 110°) is noticed with diphenylglyoxime when treated with sulfuric acid.

1888

6. Polonowska, N., "Oximes of Benzil," Ber., 21, 488 (1888)

[J. Chem. Soc. (London), 54, 485 (1888)]

When benzildioxime is reduced with sodium amalgam, tetraphenylaldine and ammonia are formed. The yield of tetraphenylaldine is small.

7. Günther, E., "Intramolecular Change in Benzildioxime," Ber.,

21, 516 (1888) [J. Chem. Soc. (London), 54, 485 (1888)]

When benzildioxime is heated with a solution of hydrogen chloride in glacial acetic acid and acetic anhydride, a diacetyl-compound is formed which, when saponified, yields Goldschmidt's isobenzildioxime, melting at 206° (Goldschmidt, Ber., 16, 2176 (1883)).

The compound (m.p. 121-122°) obtained by the action of phosphorus pentachloride on benzildioxime (Beckmann, Ber., 20, 1507 (1887)) is a dichloride, NCl:CPh.CPh:NCl ; two other nitrogenous compounds melting at 146° and 95°, respectively, are also formed in the reaction. The chloride could not be obtained from isobenzildioxime.

8. Auwers, K., and Meyer, V., "Investigation of the Second

van't Hoff Hypothesis," Ber., 21, 784 (1888) [J. Chem. Soc. (London), 54, 597 (1888)]

The authors have investigated the two isomeric benzildioximes discovered by Goldschmidt and Meyer (G. and M., Ber., 16, 1616 (1883); G., Ibid., 2176) because their existence would be a direct contradiction to van't Hoff's second hypothesis (that two carbon atoms united by a single affinity are free to rotate, the axis of rotation being the bond of union, and that isomerism is only possible for those substances of the type $\text{C}\equiv\text{C}$ which cannot by rotation around the common axis be converted into the same form).

The α -dioxime (I) is prepared from benzil and hydroxylamine hydrochloride in an alcoholic solution. The β -isomer (II) is obtained by heating I in absolute alcohol at 170-190°.

Both dioximes yield diacetyl-derivatives when treated with acetic anhydride. The derivatives, when treated with alkalies, give up the oximes from which they were prepared. The non-existence of nitroso-groups is, therefore, confirmed.

To further remove all doubt as to the possibility of merely physical isomerism and to prove that the oximes not only differ from one another, but also yield different derivatives, the propionic and isobutyric derivatives were prepared.

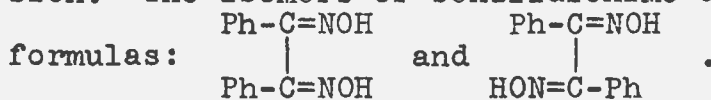
The two oximes were oxidized with potassium ferricyanide and both give the same oxidation product. Both yield the same anhydride when heated in a sealed tube with water at 200°. The molecular weight by Raoult's method gives practically the same value.

By these results, the authors thought it necessary to alter van't Hoff's second hypothesis or otherwise no explanation of isomerism of benzildioxime would be possible.

Physical properties of most derivatives cited are given.

9. Meyer, V., and Riecke, E., "The Carbon Atom and Valency," Ber., 21, 946 (1888) [J. Chem. Soc. (London), 54, 549 (1888)]7.

The authors discuss van't Hoff's and Wislicenus' conclusions (Chem. Zentr., 58, 1005 (1887)). The results are two new ideas: The valencies of the carbon atom can be diverted from the regular tetrahedron in which they are supposed to exist. And there are two ways a carbon atom can be united, one allows free rotation and one does not. They present a thorough discussion. The isomers of benzildioxime are given the



10. Auwers, K., and Meyer, V., "Isomerism of the Benzildioximes," Ber., 21, 3510 (1888) [J. Chem. Soc. (London), 56, 403 (1889)]7.

When α -benzildioxime (I) is treated with methyl iodide, α -benzildioxime dimethyl ether (II) with the composition $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2$, a non-ethereal isomer (III) of

the same composition, benzil (IV), and a base, $C_{16}H_{14}N_2$, (V) are formed. The method is described in detail (compare Japp and Klingemann, Ann., 247, 201 (1888)), and the means of separating the products are given. II reacts with hydrochloric acid to form $C_{16}H_{16}N_2O_2.HCl$ (VI) which in turn decomposes in cold water with the evolution of a gas. With strong hydrochloric acid at 100° , II is converted to IV and methylhydroxylamine (VII) in ten hours. Both II and III yield dibenzyl (VIII) when reduced with phosphorus and hydriodic acid.

β -Benzildioxime (IX) reacts in a similar manner yielding a β -ethereal (X) and β -non-ethereal (XI) isomer, IV, and V. X reacts with hydrochloric acid and the product resembles VI. Both X and XI yield VIII as the α -isomer does, and when X is heated with strong hydrochloric acid the products are IV and VII.

When III is heated at 100° for ten hours with strong hydrochloric acid, it is converted to XI, and at 170° XI is converted to benzoic acid and ammonia.

II decomposes at 170 - 180° in alcohol while III remains unchanged at 240 - 250° .

The authors also report that when I and IX are reduced with zinc-dust and aqueous soda, tetraphenylaldine, IV, and a non-nitrogenous substance are obtained.

Physical properties are given for all isomers and derivatives cited.

1889

11. Günther, E., "Intramolecular Change of α - and β -

Benzildioxime, α -Benzilmonoxime, and Deoxybenzoinoxime,"

Ann., 252, 44 (1889) [J. Chem. Soc. (London), 56, 1067 (1889)]7.

The author has previously pointed out (Ber., 21, 516 (1888)) that α -benzildioxime yields the diacetate of β -benzildioxime when it is heated with a solution of hydrogen chloride in glacial acetic acid and acetic anhydride. If acetic anhydride is omitted from the mixture, β -benzildioxime and dibenzenylazoxime are the chief products of the reaction. Dibenzenylazoxime is also formed by the action of strong sulfuric acid, phosphoric anhydride, and phosphorus oxychloride on α -benzildioxime. Phosphorus pentachloride at the ordinary temperature yields a similar result, but at a

higher temperature a dichloride, $C_{14}H_{10}N_2Cl_2$ (G., Ibid.), is formed. The chloride is decomposed by water, yielding benzamide. Silver nitrate eliminates the chlorine from the dichloride and forms a crystalline compound, $C_{14}H_{10}N_2O \cdot AgNO_3$, soluble in alcohol.

β -Benzildioxime yields a small quantity of dibenzylazoxime when treated with a solution of hydrogen chloride in acetic acid and acetic anhydride, and is converted into oxanilide by phosphorus pentoxide or pentachloride.

12. Auwers, K., and Meyer, V., "Two Isomeric Benzilemonoximes," Ber., 22, 537 (1889) [J. Chem. Soc. (London), 56, 611 (1889)]_7.

The authors report that α -benziledioxime is formed together with small quantities of lower melting compounds when α -benzilemonoxime is treated with hydroxylamine hydrochloride and soda in aqueous solution.

13. Auwers, K., and Meyer, V., "Isomerism of Oximido-compounds. Isomeric Monosubstituted Hydroxylamines," Ber., 22, 564 (1889) [J. Chem. Soc. (London), 56, 609 (1889)]_7.

α -Benziledioxime yields two benzyl-derivatives which, in their properties, show complete analogy to the two dimethyl-derivatives of the α -dioxime (compare A. and M., Ber., 21, 3510 (1888)). The one melts at $104-105^\circ$, combines with concentrated hydrochloric acid, and yields benzile when heated at 100° with concentrated hydrochloric acid. The other melts at $153-154^\circ$, does not combine with hydrochloric acid, and is converted into the corresponding dibenzyl-derivative of β -benziledioxime when treated with hydrochloric acid at 100° . The last-named compound melts at $59-60^\circ$, and is formed in considerable quantities when β -benziledioxime is treated with soda and benzyl chloride.

14. Auwers, K., and Meyer, V., "The Third Benziledioxime," Ber., 22, 705 (1889) [J. Chem. Soc. (London), 56, 713 (1889)]_7.

γ -Benziledioxime is prepared from hydroxylamine hydrochloride and the γ -monoxime, previously described as the β -monoxime (A. and M., Ber., 21, 3510 (1888)). Small quantities of the α - and $\alpha\beta$ -dioximes are also formed. A detailed procedure is given.

The γ -isomer is converted into the β -isomer (m.p. 207°) when heated to 200° . Strong hydrochloric acid at 100° also causes the conversion, but it then decomposes to benzile and hydroxylamine hydrochloride.

The diacetyl-, dipropionyl-, and diisopropyl-derivatives were prepared (compare A. and M., Ber., 21, 784 (1888)).

The physical properties of the derivatives are given, and the bearing of the results on the authors' views of stereo-chemical isomers is discussed (compare A. and M., Ibid.). The authors also use a new notation, $\alpha\beta$ -dioxime.

15. Beckmann, E., "Benzaldoximes," Ber., 22, 1588 (1889) [J.

Chem. Soc. (London), 56, 980 (1889)]

When either α - or β -benzildioxime in ethereal solution is oxidized by means of nitrous fumes, a compound is obtained which crystallizes in reddish-yellow forms, melts at 114 - 115° , and is not reduced by boiling with alcoholic ammonium sulfide or by heating with concentrated hydriodic acid at 100° . A second compound, melting at a temperature above 200° , is also produced in the oxidation, and after the reaction can be extracted from the ethereal solution by means of aqueous alkali.

16. Goldschmidt, H., "Oximes," Ber., 22, 3101 (1889) [J. Chem.

Soc. (London), 58, 251 (1890)]

The three isomers of benzildioxime are reacted with phenyl cyanate. Goldschmidt concludes that the oximido-groups of all three isomers are the same and, therefore, the isomerism is stereochemical.

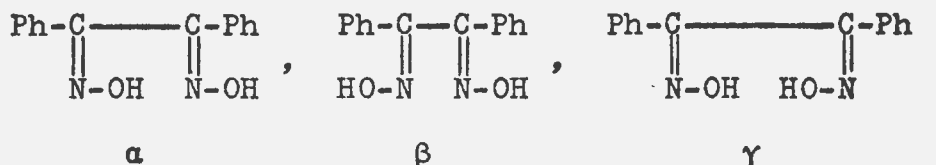
1890

17. Hantzsch, A., and Werner, A., "Arrangement in Space of the Atoms in the Molecule of Carbon Compounds Containing

Nitrogen," Ber., 23, 11 (1890) [J. Chem. Soc. (London), 58, 348 (1890)].

The theories of Auwers and Meyer (Ber., 21, 784 (1888)), Beckmann (Ber., 22, 514 (1889)), and Goldschmidt (Ber., 22, 3101 (1889)) on isomerism are discussed.

The principles of the tetrahedral carbon atom are applied to nitrogen and it is assumed that nitrogen forms an irregular tetrahedron with the fourth corner occupied by the atom itself. From this assumption the following formulas are given:



The reasoning behind these structures and the possibility of more existing isomers are discussed. Experiments were in progress to see if isomers of ammonia or hydrazine could exist in order to confirm

this theory, i.e., optical isomers of $\text{N} \begin{array}{l} \nearrow \text{R}_1 \\ \rightarrow \text{R}_2 \\ \searrow \text{R}_3 \end{array}$.

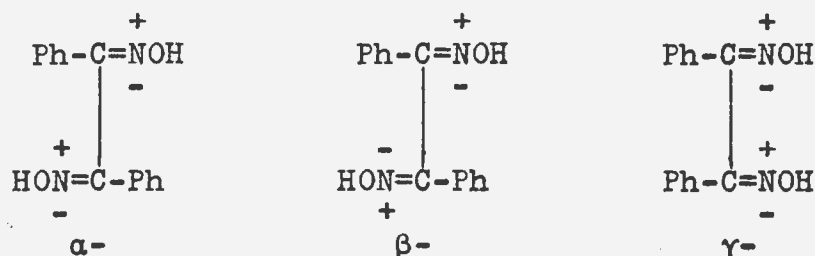
18. Behrend, R., "Stereochemistry of Nitrogenous Compounds,"

Ber., 23, 454 (1890) [J. Chem. Soc. (London), 58, 575 (1890)].

The author obtained results and formulated theories on alkyl-derivatives of hydroxylamine which conflict with the theories of Hantzsch and Werner (Ber., 23, 11 (1890)).

Through the central points of the atoms or groups of atoms combined with nitrogen in ammonia or substituted ammonias, a plane may always be imagined to pass. Ammonia can also unite simultaneously with a positive and negative element, and it is assumed that these take up positions on either side of the plane at previously fixed points, i.e., a negative and positive pole. In conclusion, ammonium salts would have the same relationship to each other as active tartaric acids. Although none have been found, it was supposed that the isomers pass into a state of equilibrium. In favor of this theory were the ammonium bases prepared by Meyer and Lecco (Ber., 8, 936 (1875)).

The isomerism of the benzildioximes is explained under this equilibrium assumption because the carbon atom can rotate freely, and the equilibrium is influenced by the attraction of the attached groups.



19. Meyer, V., "Results and Aims of Stereochemical Research," Ber., 23, 567 (1890) [J. Chem. Soc. (London), 58, 719 (1890)]

The author summarizes all work done so far on isomerism and comments on the results and theories. He urges the use of space formulas in dealing with the problem.

20. Dittrich, M., "Ethers of Benziloximes," Ber., 23, 3589 (1890) [J. Chem. Soc. (London), 60, 317 (1891)]

Attempts to prepare the methyl ether of γ -benzildioxime (compare Auwers and Meyer, Ber., 21, 3510 (1888)) resulted in the formation of products of the more stable β -dioxime. The melting point of the hydrochloride is given as 140-143°, instead of 130° (A. and M., Ibid.).

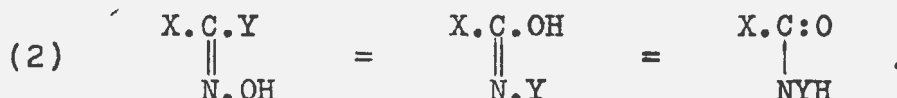
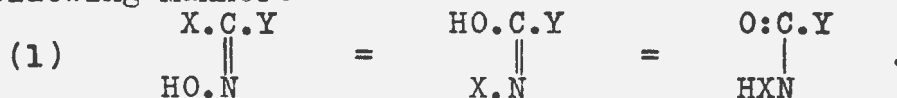
A β -methylhydroxylamine which was prepared from β -benzildioxime methyl ether and hydrochloric acid is reported.

By the action of α -benzylhydroxylamine on γ -benzilemonoxime benzyl ether at 130-150°, a dibenzyl ether of α -benziledioxime is formed. The same compound is formed from α -benzylhydroxylamine and α -benzilemonoxime. Similar experiments with β -benzylhydroxylamine give negative results. The non-basic methyl ether of α -benziledioxime does not react with methyl iodide while the second modification reacts with methyl iodide at 100° to yield α -benziloxime methyl ether. The second modification also yields methyl iodide and ammonia with hydriodic acid at 200°. These results show that the α -benziledioxime methyl ethers are structural isomers.

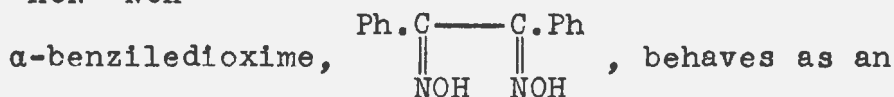
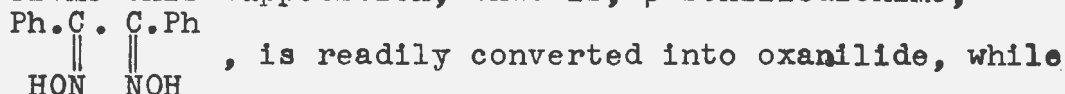
1891

21. Hantzsch, A., "Determination of the Spatial Configuration of Stereo-isomeric Oximes," Ber., 24, 13 (1891); (see also H. and Werner, Ber., 23, 11 (1890); H. and W., Ibid., 1243; H., Ibid., 2325; Auwers and Meyer, Ibid., 2403) [J. Chem. Soc. (London), 60, 439 (1891)]

The author discusses the work which has been done on aldoximes and ketoximes relating to stereo-isomerism and intramolecular changes. In regard to the intramolecular change in oximes, he represents the change in the following manner:



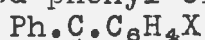
The behavior of the benziledioximes likewise confirms this supposition, that is, β -benziledioxime,



asymmetrical compound in Beckmann's reaction (Ber., 23, 1680 (1890)).

In the case of stereo-isomeric ketoximes it is, therefore, possible to determine the configuration by means of the acid amide which it forms in Beckmann's reaction, the hydroxyl group being closer to the radical which is found combined with the nitrogen in the amide.

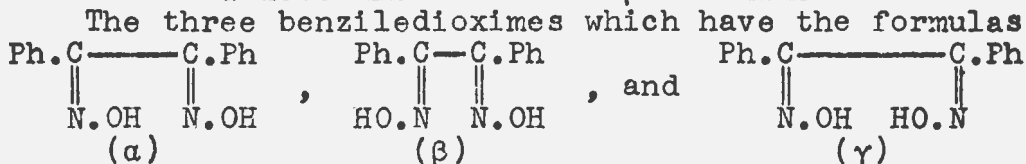
In view of the results obtained by the author, the prefix α - is proposed for those ketoximes in which the hydroxyl occupies the adjacent position to the unsubstituted phenyl or other radical:



α -ketoxime



β -ketoxime



become $\alpha\beta$ -, $\alpha\alpha$ -, and $\beta\beta$ -benziledioxime.

Hantzsch also states that in all the reactions which he has performed, the hydroxyl group takes part as a whole, and not simply the hydrogen atom. This is not in agreement with Auwers and Meyer (loc. cit.).

22. Dodge, F. D., "Diphenylfurazan and Some Derivatives of Oximes," Ann., 264, 178 (1891) [J. Chem. Soc. (London), 60, 1237 (1891)]

Diphenylfurazan, prepared by heating α -benziledioxime with water at 200-210° (compare Auwers and Meyer, Ber., 21, 784 (1888)), melts at 94°, and distills with partial decomposition, yielding benzonitrile, phenylcarbimide, and a compound melting at 110°, which is in all probability dibenzerylazoxime, identical with the substance obtained by Beckmann by the action of sulfuric acid on α -benziledioxime.

An energetic reaction takes place when α -benziledioxime is heated with phosphorus pentasulfide; benzonitrile and small quantities of dibenzerylazoxime are formed, but diphenylfurazan is not produced.

23. Claus, A., "Oximes and So-called Stereochemistry," J. prakt. Chem. (2), 44, 312 (1891) [J. Chem. Soc. (London), 62, 50 (1892)]

This paper deals with the isomerism of the hydroxylamine derivatives of benzile, and especially with the recent work of Auwers and Meyer on the subject (Ber., 21, 3510 (1888); Ber., 22, 537 (1889); Ibid., 564; Ibid., 705). The author concludes by claiming that he has incontrovertibly proved that all manifestations of isomerism among the products of the reaction of hydroxylamine with benzile can be efficiently and easily explained as cases of isomerism in structure, without having recourse to any stereochemical hypothesis.

24. Auwers, K., and Meyer, V., "Claus' Theory of the Benziloximes," Ber., 24, 3267 (1891) [J. Chem. Soc. (London), 62, 186 (1892)]

Auwers and Meyer discuss Claus' views on benziloximes (J. prakt. Chem. (2), 44, 312 (1891)). The three benzildioximes are regarded as stereochemical isomers since it has been shown that they have the same structure. Claus differs in his theory by regarding the isomers as having different molecular structures.

1892

25. Claus, A., "Oximes and So-called Stereochemistry," J. prakt. Chem. (2), 45, 1 (1892) [J. Chem. Soc. (London), 62, 598 (1892)]7.

The author replies to Auwers and Meyer (Ber., 24, 3267 (1891)), who have criticized his previous paper on the subject (J. prakt. Chem. (2), 44, 312 (1891)), and maintains his former position. The paper contains no new facts.

26. Minunni, G., and Ortoleva, G., "Benzileoximes," Gazz. chim. ital., 22 (2), 183 (1892) [J. Chem. Soc. (London), 64 (1), 97 (1893)]7.

α -Benziledioxime (5 g.), when heated with phenylhydrazine (4.5 g.) at 150-160°, gives off ammonia, and, by treating the cooled mass with alcohol, unaltered dioxime and benziledihydrazone are obtained. On heating the dioxime (2 g.) with a large excess (10 g.) of phenylhydrazine at 170° for some hours, complete conversion into β -benziledioxime occurs; the latter then combines with the phenylhydrazine, forming a compound of the composition

$$\begin{array}{c} \text{PhC:NH(OH)} \\ | \\ \text{PhC:NH(OH)} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{N.NHPh, which}$$

melts at 149°. On treating this with acids, it yields β -benziledioxime and phenylhydrazine.

27. Minunni, G., "Isomerism of Oximes," Gazz. chim. ital., 22 (2), 191 (1892) [J. Chem. Soc. (London), 64 (1), 89 (1893)]7.

The author considers that he has demonstrated the futility of the stereochemical hypotheses offered by

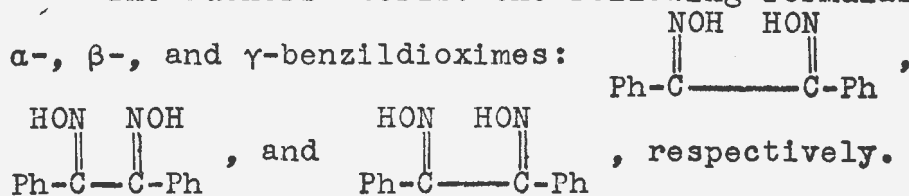
Auwers, Meyer, Hantzsch, and Werner for elucidating the isomerism of the oximes, his own theory being the only one which accords with the facts. He has shown that Hantzsch's first attack (Ber., 24, 1192 (1891)) on this theory was based on misapprehension (M., Gazz. chim. ital., 21 (2), 192 (1891)), while the constitutional formulas assigned by Claus are insufficient to explain the isomerism.

1893

28. Beckmann, E., and Köster, A., "Hydroximido-derivatives:

Benzileoximes," Ann., 274, 1 (1893) [Chem. Zentr., 64 (1), 938 (1893); J. Chem. Soc. (London), 64 (1), 474 (1893)]7.

The authors ascribe the following formulas to the α -, β -, and γ -benzildioximes:



α -Benzildioxime yields dibenzenylazoxime (I) and isobenzenylazoxime when treated with phosphorus pentachloride (II), phosphorus pentabromide (III), phosphorus oxychloride (IV), or sulfuric acid (V) (compare Günther, Ann., 252, 44 (1889)). β -Benzildioxime is converted to oxanilide by II (G., Ibid.), and to oxanilideparasulfonic acid by V. γ -Benzildioxime reacts with II, IV, and V to give I, benzoylphenylcarbamide, or their decomposition products. γ -Benzildioxime is converted to the α -isomer when treated with acetic anhydride and hydrogen chloride, and to the β -isomer when heated with alkali. Both α - and γ -benzildioxime form the β -isomer more easily than the normal anhydride (m.p. 94°), and the γ -diacetyl derivative only forms the anhydride. The α -isomer forms the anhydrides as mentioned above and neither anhydride is considered the normal anhydride.

29. Claus, A., "Oximes," J. prakt. Chem. (2), 47, 139 (1893)

[J. Chem. Soc. (London), 64 (1), 355 (1893)]7.

A criticism on the most recent papers of Minunni (Gazz. chim. ital., 22 (2), 183 (1892); Ibid., 191; Ibid., 213; Ibid., 230; compare C., J. prakt. Chem. (2), 45, 556 (1892)).

30. Minunni, G., and Ortoleva, G., "Two Recent Publications on the Benzileoximes," Gazz. chim. ital., 23 (2), 244 (1893) [J. Chem. Soc. (London), 66 (1), 135 (1894)]

This paper deals with the criticisms of Auwers and Siegfeld (Ber., 26, 788 (1893)) and of Claus (J. prakt. Chem. (2), 47, 139 (1893)) on the authors' work (Gazz. chim. ital., 22 (2), 183 (1892)).

1894

31. Feist, F., "Reduction of Benziledioximes," Ber., 27, 213 (1894) [J. Chem. Soc. (London), 66 (1), 196 (1894)]

Diphenylethylenediamine, $\text{NH}_2\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NH}_2$, was obtained, after several unsuccessful attempts, from both α - and β -benziledioxime, by reducing them with metallic sodium in ethyl-alcoholic solution. It forms white, feathery crystals, and melts at 90-92°. The white hydrochloride, $\text{C}_{14}\text{H}_{16}\text{N}_2\cdot 2\text{HCl} + 2\text{H}_2\text{O}$, melts with decomposition at 248°; the yellow picrate, $\text{C}_{14}\text{H}_{16}\text{N}_2\cdot 2\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, at 220°; the yellow platinochloride, $\text{C}_{14}\text{H}_{16}\text{N}_2\cdot \text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$, decomposes at 222-225° without melting.

1900

32. Petrenko-Kritschenko, P. Iw., and Kasanezky, P., "Ketoximes," Ber., 33, 854 (1900); (compare P.-K. and Rosenzweig, Ber., 32, 1744 (1899)) [J. Chem. Soc. (London), 78 (1), 350 (1900)]

Other oximes besides the one already investigated, orthodiethoxydiphenyltetrahydropyrone (P.-K. and R., loc. cit.), form double compounds with certain solvents. β -Benzildioxime crystallizes with ethylene glycol (1.5 moles), glycerol (0.5 mole), benzene (1 mole), acetic acid (1.5 moles), aniline (2 moles), pyridine (2 moles), and acetone (1 mole).

1903

33. Whiteley, M. A., "The Oxime of Mesoxamide and Some Allied Compounds. II. Disubstituted Derivatives," J. Chem. Soc. (London), 83, 24 (1903).

The possibility that the hydrogen of the oximino-group is acidic is the basis of this investigation. The formation of yellow alkali salts is characteristic of α -oximinoketones. Schramm (Ber., 16, 183 (1883)) first drew attention to the influence of a neighboring radical on the acid character of the oximino-group, and later it is pointed out that the alkali salts yield yellow colored compounds from open chain compounds and red to violet colored compounds from ring compounds. The purple or blue ferrous salts are much more characteristic. α -Oximinoketones were prepared and examined. The two monoximes of benzil exhibit isomerism, and one of these forms no ferrous salt of characteristic color.

Attention was directed to the stereoisomeric oximes and the dioximes of benzil. These compounds give a pale yellow color with alkali and they show a difference in behavior on the further addition of Fe^{++} . α -Benzildioxime gives a rich, purple color, β -benzildioxime gives no trace of color, and γ -benzildioxime gives a reddish-purple color changing rapidly to the dark brown of ferric hydroxide. Representing these by the formulas assigned by Beckmann and Köster (Ann., 274, 32 (1893)), it can be seen that the syn-isomer forms a stable salt, the amphi-isomer an unstable salt, and the anti-isomer forms none.

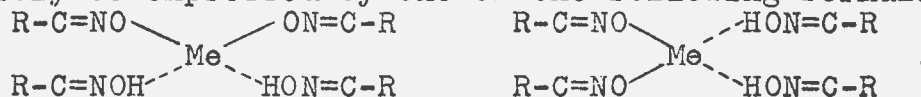
These compounds present further interest in that they are diketones and they yield yellow alkali salts and one of them yields a purple Fe^{++} salt. This indicates that the radical $=\text{C}:\text{N}.\text{OH}$, like carbonyl, can sometimes influence the acidic nature of a contiguous oximino-group. This conclusion is opposed to that of Schramm (loc. cit.) who attributed the non-formation of colored alkali salts from methylglyoxime to the inoperative character of the two oximino groups as compared with the color-giving property of the carbonyl, oximino-group in isonitrosoacetone.

1905

34. Tschugaeff, L., "Complex Compounds of α -Dioximes," Z. anorg. Chem., 46, 144 (1905) [J. Chem. Soc. (London), 88 (1), 743 (1905)].

The α -dioximes differ from all others in reacting with nickel, cobalt, iron, platinum, palladium, and copper salts to form stable salts, called by the author dioximines. Nickel diphenylglyoximine, $C_{24}H_{22}O_4N_4Ni$, formed from nickel acetate and α -benzildioxime, melts and decomposes at 300° . Platinodiphenylglyoximine, $C_{28}H_{22}O_4N_4Pt$, is best obtained by digesting platinum-cis-dichloropyridine with α -benzildioxime in aqueous acetic acid solution. It forms reddish-brown needles which are decomposed by heating to a high temperature, are only very slightly volatile even in a vacuum, and dissolve very sparingly in organic solvents. Palladodiphenylglyoximine, prepared by adding a concentrated aqueous solution of palladium ammonium chloride to a solution of α -benzildioxime in pyridine, has not been further examined.

If it is assumed that in the dioximine molecule not only the $=NO$ but also the $=NOH$ residue is in direct union with the metal, then the assumption must also be made that in these compounds cyclic atomic unions are present. Thus, the construction of the dioximines may possibly be expressed by one of the following formulas:

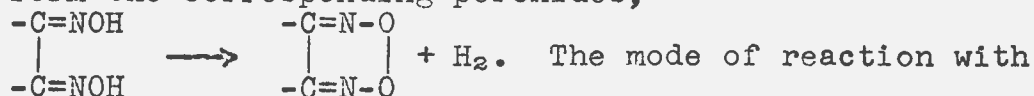


The stability of the dioximines is consistent with a cyclic formula.

1906

35. Ponzio, G. "Behavior of Acetoxime and of Dioximes Towards Sodium Hypochloride. Properties of Carbon Tetrabromide," Atti reale accad. sci. Torino, 41, 415 (1906) [J. Chem. Soc. (London), 90 (1), 482 (1906)].

With sodium hypochloride, the dioximes of benzyl form the corresponding peroxides,



sodium hypochloride is, therefore, similar to that of potassium ferricyanide (compare Auwers and Meyer, Ber., 22, 705 (1889)). Advantages in using the hypochloride are: oxidation takes place almost instantaneously and in the cold, a theoretical yield is obtained, and the products do not require tedious purification which is necessary when ferricyanide is employed.

1908

36. Tschugaeff, L. "Method for the Determination of the Configuration of α -Dioximes," Ber., 41, 1678 (1908); (compare T., Z. anorg. Chem., 46, 144 (1905)) [J. Chem. Soc. (London), 94 (1), 554 (1908)].

The fact that, of the various stereoisomerides of an α -dioxime, the syn-modification alone yields complex metallic dioximes is utilized for the determination of the configuration of dioximes. Stierlin's α -anisildioxime (Ber., 22, 376 (1889)), Hoffmann's α -cuminildioxime (Ber., 23, 2064 (1890)), and α -furildioxime (m.p. 166-168°) are thus shown to possess the syn-configuration, while Werner and Bloch's two stereoisomeric o:o'-dichlorobenzildioxime (Ber., 32, 1975 (1899)), which do not form colored complex metallic derivatives, must be the amphi- and the anti-modifications.

An interesting illustration of the method is given by Boeris' stereoisomeric methylanisylglyoxaldioximes (Gazz. chim. ital., 23 (2), 165 (1893)).

1911

37. Chugaev, L., and Koch, P., "Anomaly of the Molecular Refraction in the Substituted Glyoxime Series," Compt. rend., 153, 259 (1911) [CA, 6, 599 (1912)].

The molecular refraction of disubstituted dioximes exhibits an abnormally high value when two =NOH groups are in the α -position. If the substituents are aliphatic, the increase amounts to 1.3; if aromatic, it is much greater. With the =NOH groups in the β - or γ -positions the abnormality vanishes. This behavior is similar to that of other conjugate double linkages.

The molar refraction for anti-benzildioxime dissolved in pyridine was found experimentally to be 72.32. The calculated value was 68.87.

1912

38. Biltz, H., and Krebs, P., "Reductions in the Glyoxaline Series. II. Reduction of Thiodiphenylglyoxalone,"

Ann., 391, 191 (1912) [J. Chem. Soc. (London), 102 (1), 908 (1912)]

The authors obtained results similar to Feist (Ber., 27, 213 (1894)) upon the reduction of α -benzildioxime with sodium in alcohol.

39. Garner, W. E., "Dioximes of Benzil," Chem. News, 106, 202 (1912) [J. Chem. Soc. (London), 102 (1), 995 (1912)]

The usual method of formulation of the three dioximes of benzil does not readily account for the fact that the γ -oxime loses water more readily than the α -oxime with formation of diphenylfurazan, but it is shown that if the two hydroxyl groups lie outside the plane of the remainder of the molecule these difficulties are removed.

1913

40. Atack, F. W., "The Detection and Estimation of Nickel by Means of α -Benzildioxime," Chemiker-Ztg., 37, 773 (1913); Analyst, 38, 316 (1913); J. Chem. Soc. (London), 103, 1317 (1913) [CA, 7, 3291 (1913); Chem. Zentr., 84 (2), 1307 (1913); Z. anal. Chem., 53, 620 (1914)]

A 0.02% alcohol or acetone solution of α -benzildioxime which has been made somewhat ammoniacal will immediately produce a copious intensely red precipitate of $C_2H_{22}N_4O_4Ni$ with a solution containing 0.002 mg. nickel in 5 cc. (1 part in 2,000,000). Ten cc. of an ammoniacal solution containing 1 part per 1,000,000 of nickel and 100 times that amount of cobalt gives a distinct and immediate test for nickel. Iron, silver, magnesium, chromium, and manganese do not interfere with the qualitative determination. Large amounts of nitrates seriously affect the determination and must be removed by evaporating with sulfuric acid before adding the reagent. In the quantitative determinations amounts containing less than 0.025 g. nickel should be used. A slight excess of a warm solution of the reagent in alcohol, to which ammonia has been added, is added with stirring to the ammoniacal nickel

solution and warmed for a few moments on the water bath. Precipitation is complete in one minute. It is filtered on a Gooch crucible, washed with 50% alcohol and hot water, and dried at 110°. The precipitate contains 10.93% nickel. Directions for the quantitative determination of nickel in the presence of other metals are given. α -Benzildioxime is made by boiling 10 g. benzil (not necessarily pure) with 8-10 g. hydroxylamine hydrochloride in methanol solution; after boiling three hours the precipitate is filtered off, dried, washed with hot water, then a small amount of 50% alcohol, and dried, when it consists of pure α -benzildioxime (m.p. 237°). A further yield may be obtained by boiling the filtrate with hydroxylamine hydrochloride.

1916

41. Kelley, G. L., and Conant, J. B., "The Use of Diphenylglyoxime as an Indicator in the Volumetric Determination of Nickel by Frevert's Method," J. Ind. Eng. Chem., 8, 804 (1916) [CA, 10, 2675 (1916)].

The nickel in the sample is precipitated as the dimethylglyoxime compound. The complex is destroyed by baking in potassium perchlorate and then, after neutralization, an excess of standard potassium thiocyanate is titrated with nickel sulfate and diphenylglyoxime is used to mark the end point. Diphenylglyoxime was found superior to dimethylglyoxime because it could be used in lower concentration due to the lower solubility of its nickel complex.

It was found that the chloride, nitrate, and sulfate salts of sodium, potassium, and ammonia caused the indicator to precipitate. Strongly alkaline solutions caused no reaction between the nickel salt and the indicator. Ammonia present in greater concentration than 2% made the end point unsatisfactory.

42. Angeli, A., "Configuration of Certain Glyoximes," Atti. reale accad. Lincei (2), 25, 7 (1916) [J. Chem. Soc. (London), 110 (1), 655 (1916)].

The author discusses the configuration of the peroxides which has been given to the glyoximes. Contrary to Wieland and Semper (Ann., 358, 36 (1908)), he finds that these peroxides react readily with Grignard reagent in either ethereal or benzene solution. The results are in agreement with Green and Rowe's formulas (J. Chem. Soc. (London), 103, 897 (1913)).

When benzildioxime reacts with phosphorus pentachloride, the reaction is very energetic and further chlorinated products are probably formed as intermediates. The author states that if the transposition followed by Beckmann and Köster (Ann., 274, 1 (1893)) is to be employed to determine the configuration of the glyoximes, the manner in which it proceeds must first be definitely established, because the study of ethylenic compounds shows that intramolecular reactions in the cis-position are not always preferred.

1917

43. Koppel J., "Specific Reactions for Analytical Chemistry," Naturwissenschaften, 5, 730 (1917) [Chem. Zentr., 89 (1), 239 (1918)]_7.

The author reports that benzildioxime is a specific reagent for the determination of nickel.

44. Chapman, C., "Some Main Lines of Advance in the Domain of Modern Analytical Chemistry," J. Chem. Soc. (London), 111, 203 (1917).

The dioxime, α -benzildioxime, described by Tschugaev has been recommended by Atack for the qualitative detection of nickel. It forms an intensely red compound having the formula $C_{20}H_{22}O_4N_4Ni$ containing 10.9% nickel. The sensitivity is greater than the sensitivity of dimethylglyoxime and it has been stated that one part nickel in ten million of water can be detected. α -Benzildioxime can also detect one part nickel in five million parts of hardened edible fats in which nickel has been used as a catalyst.

45. Grossmann, H., and Mannheim, J., " α -Benzildioxime (Reagent for Nickel)," Ber., 50, 708 (1917) [CA, 11, 3190 (1917)]; J. Chem. Soc. (London), 112 (2), 391 (1917) 7.

The authors have tested Atack's method for detecting and estimating nickel in which α -benzildioxime is the precipitant (cf. A., Chemiker-Ztg., 37, 773 (1913)). The reagent is best prepared by warming a methanol solution of benzil with powdered hydroxylamine hydrochloride and a few drops of hydrochloric acid, the oxime being filtered off from time to time. It is applied in the form of a saturated, alcoholic solution. For the separation of nickel from zinc or magnesium, ammonium chloride is added; manganese is retained in solution by means of citric acid and hydrazine (to prevent oxidation); copper is kept in solution by means of Rochelle salt, but only small proportions should be present. The nickel precipitate does not suffer loss of weight even at 180°.

46. Auwers, K., "Preparation of α -Benzil Dioxime," Ber., 50, 952 (1917) [CA, 12, 693 (1918)]; J. Chem. Soc. (London), 112 (1), 572 (1917) 7.

The process suggested by Grossmann and Mannheim (Ber., 50, 708 (1917)) was already described by Auwers in 1888, and Atack's method (Chemiker-Ztg., 37, 773 (1913)) is not so unsuitable as supposed by Grossmann and Mannheim.

1918

47. Strebinger, R., "Estimation of Ions by Microanalytical Methods. I.," Osterr. Chemiker-Ztg., 21, 71 (1918) [Chem. Zentr., 89 (2), 471 (1918)]; J. Chem. Soc. (London), 116 (2), 34 (1919); CA, 14, 703 (1920) 7.

Strebinger has extended Pregl's method of quantitative organic microanalysis to inorganic substances, and describes the estimation of silver, nickel, arsenic, iron, chromium, and copper, and the separations of silver from copper and lead from tin. Precipitation of nickel with α -benzildioxime is unsuitable for microanalytical purposes, the results being too high.


48. Strebinger, R., "Estimation of Nickel with α -Benzildioxime,"
Chemiker-Ztg., 42, 242 (1918) [CA, 12, 2175 (1918);
J. Chem. Soc. (London), 114 (2), 243 (1918)]_7.

Strebinger agrees with Grossmann and Mannheim (Ber., 50, 708 (1917)) that Attack's method of estimating nickel by precipitation with α -benzildioxime is trustworthy for small quantities of the metal. When, however, the quantity of nickel exceeds 0.025 g., the precipitate contains a certain amount of occluded α -benzildioxime, and the results obtained are too high. In such cases, the precipitate should be ignited and the resulting nickel oxide weighed.

1921

49. Attack, F. W., "Structural Isomerism of the Oximes. I. Criticism of the Hantzsch-Werner Hypothesis and a New Theory of the Constitution of Isomeric Oximes," J. Chem. Soc. (London), 119, 1175 (1921) [CA, 15, 3091 (1921)]_7.

The Hantzsch-Werner hypothesis of the stereoisomerism of oximes is criticized in view of the fact that it fails to explain characteristic reactions of the so-called syn- and anti-oximes, their mode of interconversion, etc., and further fails to interpret the Beckmann reaction as applied to the benzildioximes. The new theory proposed by Attack depends essentially on the existence of a generally unstable modification ($=C:N(:O)H$, "nitrone") containing quinquivalent nitrogen, intermediate between the two usually stable

isomers ($=C:NOH$, "oxime," and , "isoöxime")

containing tervalent nitrogen. While the last two represent groups of sufficient stability to enable compounds containing them to be isolated in the free state, it would be expected that in suitable circumstances there would be a possibility of isolating the third isomeric oxime having the "nitrone" formula. An explanation, using this theory, is made of the number of isomerides known to exist, the difference in the salt-forming properties of the oxime groups present in isomeric oximes, and the formation of O- and N-ether, respectively, from isomeric oximes.

50. Atack, F. W., and Whinyates, L., "Structural Isomerism of the Oximes. II. A Fourth Benzil Dioxime," J. Chem. Soc. (London), 119, 1184 (1921) [CA, 15, 3091 (1921)].

δ -Benzildioxime is prepared by dissolving 0.5 g. α -benzildioxime in 20 cc. cold sodium hydroxide, allowing it to stand two hours, diluting with an equal volume water, and adding ammonium chloride. The powder melts at 217°. If the reaction product of hydroxylamine hydrochloride upon α -benzil monoxime in sodium hydroxide solution, is precipitated with ammonium chloride, the new isomer is also obtained. The δ -isomer is characterized by the formation of a buff-colored nickel compound on the addition of an ammonium hydroxide solution of a nickel salt to the sodium hydroxide solution. It differs by the facility with which it passes into the red nickel compound of α -benzildioxime. The δ -isomer is unstable in solvents, and passes rapidly in alcohol in the presence of acids or ammonia into the α -isomer.

51. Meisenheimer, J., "The Beckmann Transformation," Ber., 54B, 3206 (1921) [J. Chem. Soc. (London), 122 (1), 152 (1922); CA, 16, 2105 (1922)].

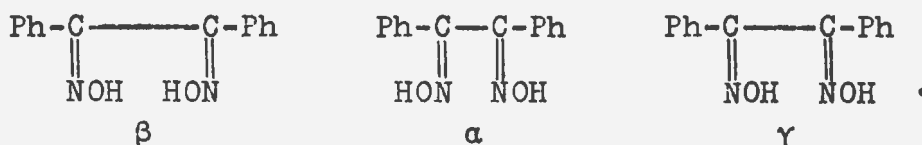
In accordance with the Beckmann transformation and the assumption that intramolecular reactions occur more readily when reacting groups are near one another, the author notes that the following configurations have been assigned to benzilmonoxime:



The author points out that the assumption has never been proven. On the basis of the reaction of 3,4,5-triphenylisoxazole upon oxidation by chromic acid or ozone the author states that the configurations are just opposite to what had previously been supposed:



This means in the case of the benzildioximes configurations, the following configurations are the actual ones:



A review of the behavior of the dioximes shows that this arrangement is probably correct.

1923

52. Ponzio, G., and Avogadro, L., "Dioximes. IX.," Gazz. chim. ital., 53, 311 (1923) [CA, 17, 3874 (1923)]7.

α -Phenylglyoxime in cold 10% sodium hydroxide and dilute benzenediazonium chloride yields β -benzildioxime. β -Phenylglyoxime similarly yields α -benzildioxime. β -Benzildioxime treated with acetic anhydride and sodium acetate gives the diacetyl derivative (m.p. 124-5°); the aqueous ethyl alcohol solution heated with acetic acid is slowly converted to the α -dioxime.

53. Ciusa, R., and Parisi, E., "Peroxides of Monoximes," Gazz. chim. ital., 53, 667 (1923) [CA, 18, 821 (1924)]7.

In order to complete the picture of the products formed contemporaneously with the so-called peroxides of the aldioximes, Ciusa and Parisi have studied the oxidation of m-nitrobenzaloxime with "Robin's" reagent. Diphenylglyoxime peroxide, m.p. 115-6°, was found as a product.

54. Ponzio, G., "Dioximes. XV.," Gazz. chim. ital., 53, 713 (1923) [J. Chem. Soc. (London), 126 (1), 56 (1924)]7.

Isomerization of the α - into the β -forms of glyoximes may be effected to some extent by simple fusion but decomposition occurs before the change reaches completion. Contrary to the statement made by Auwers and Meyer (Ber., 21, 3510 (1888)), if benzildioxime, m.p. 207°, is heated to its melting point and then immediately cooled, it is found to have undergone partial conversion into the isomeride with m.p. 237°. Hence, in this case, as in others, the stable form of the glyoxime is that with the highest melting point, and the prefixes α - and β - should be interchanged.

55. Ponzio, G., and Bernardi, V., "Dioximes. XVI.," Gazz. chim. ital., 53, 813 (1923); cf. P., Gazz. chim. ital., 53, 713 (1923) [J. Chem. Soc. (London), 126 (1), 293 (1924)].

The formation of the two benzildioximes from the two forms of phenylglyoxime by the action of phenyldiazonium chloride (P. and Avogadro, Gazz. chim. ital., 53, 311 (1923)) appears to be a reaction of general application constituting a new method of synthesizing symmetrical and unsymmetrical, disubstituted glyoximes. Not only aryl but alkyl-aryl glyoximes can be made in this way. This reaction usually gives a 45% yield.

The physical properties are also given for some similar glyoximes.

56. Parisi, E., "New Isomeride of Wieland's Dibenzenyloxoazoxime," Atti. reale accad. Lincei, 32, 572 (1923) [J. Chem. Soc. (London), 124 (1), 1018 (1923)].

Two compounds of the formula $C_{14}H_{10}O_2N_2$ have been obtained by oxidation of benzaldoxime, namely, diphenylglyoxime peroxide and dibenzenyloxoazoxime.

Diphenylglyoxime peroxide yields no additive compound with iodine and when reduced by means of zinc and

acetic acid, gives diphenylfurazan, $\begin{array}{c} \text{N:CPh} \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{N:CPh} \end{array}$, which

may be regarded as a product of anhydride formation with benzildioxime. It is, therefore, probable that

the peroxide has the formula $\begin{array}{c} \text{N} \quad \text{CPh} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{CPh} \end{array}$ or $\begin{array}{c} \text{O.N:CPh} \\ | \\ \text{O.N:CPh} \end{array}$.

57. Tansley, L. B., "The Influence of Dilution on the Hydrolytic Dissociation of Some Oxime Hydrochlorides," J. Chem. Soc. (London), 123, 3164 (1923).

This is a study of the hydrolysis of the hydrochlorides of a number of oximes, using the

polarimetric method to determine the concentration of free acid formed at dilutions ranging from N/10 to N/160 at 55.7°. Ostwald's dilution law, Rudolphi's formula, Jahn's formula, and other theories and empirical formulas are discussed.

The degree of hydrolysis of α -benzildioxime hydrochloride is given as 93.3%. The hydrolysis constant is given as 13.92 which was calculated from $K = x/(1-x)$. The latter equation was arrived at from experimental data.

1924

58. Brady, O. L., and Dunn, F. P., "Isomerism of the Oximes.

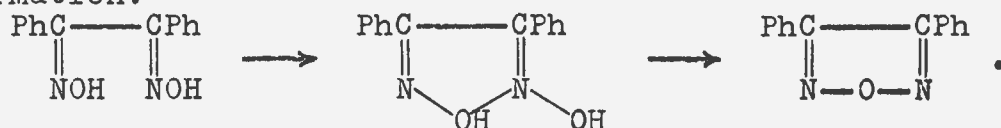
XV. The Alleged Fourth Benzil Dioxime," J. Chem. Soc. (London), 125, 291 (1924); cf. B. and Truszkowski, J. Chem. Soc. (London), 123, 2698 (1923) [CA, 18, 981 (1924)]; J. Chem. Soc. (London), 126 (1), 292 (1924)]

Efforts to repeat the work of Attack and Whinyates (J. Chem. Soc. (London), 119, 1184 (1921)), in which they claim to have isolated a fourth benzildioxime, have failed. The importance of the observation lies in the fact that Attack, on its basis, discards the Hantzsch-Werner theory and proposes a structural theory. Brady and Dunn believe that the solution of the problems involved in oxime isomerism lies in the extension of the stereochemical hypothesis rather than in its rejection.

59. Meisenheimer, J., and Lamparter, W., "Beckmann Rearrangement. II.," Ber., 57B, 276 (1924); cf. M., Ber., 54B, 3206 (1921) [CA, 18, 2153 (1924)]; J. Chem. Soc. (London), 126 (1), 432 (1924)]

The tendency of benzildioximes to lose water has been examined by heating in vacuo at 155°. The α -dioxime is volatilized most slowly, with partial transformation into the β -form; the β -dioxime sublimes more readily and unchanged, while the γ -dioxime loses water and forms an anhydride; at the same time there is transformation into the β -form and when this is complete, anhydride formation stops. This behavior is in

harmony with the behavior of the acetates, since only the γ -acetate is hydrolyzed with the production of the anhydride. The benzoyl derivatives behave similarly. The following scheme is proposed for the anhydride formation:



The α - and β -dibenzoyl derivatives (m.p. 200°, 157-8°) yield the corresponding oximes when saponified, while the γ -derivative (m.p. 135°) gives a quantitative yield of the anhydride. When benzildioxime is heated with benzoic anhydride at 70-80°, benzoyl- α -benziloxime is obtained; the excess reagent is destroyed with warm water. The diacetyl derivative of the β -dioxime gives a dimorphous substance when heated at 125-130° for 30 minutes. The presence of small amounts of the γ -isomer in this substance is indicated because small amounts of the anhydride are formed when this dimorphous substance is hydrolyzed. δ -Benzildioxime (Atack and Whinyates, J. Chem. Soc. (London), 119, 1184 (1921)) is shown to be a mixture of the α - and β -isomer.

1925

60. Purvis, J. E., "Absorption Spectra of Various Aldehydes and Ketones and Some of Their Derived Compounds," J. Chem. Soc. (London), 127, 9 (1925) [J. Chem. Soc. (London), 128 (2), 627 (1925)]_7.

α -Diphenylglyoxime shows a weak band at 2380 A. which corresponds to the very weak band of liquid diphenyl at 2300 A., described by Baly and Tryhorn (J. Chem. Soc. (London), 107, 1058 (1915)). The author discusses his results and the results of others on related compounds and states that α -diphenylglyoxime behaves like all oximes. The C=O groups are completely eliminated in the oxime and the specific absorption of the original substance is destroyed.

61. Soule, B. A., " α -Furildioxime as a Reagent for the Detection and Determination of Nickel," J. Am. Chem. Soc., 47, 981 (1925) [CA, 19, 1548 (1925)]_7.

α -Furildioxime is reported as a more sensitive precipitant for nickel than α -benzildioxime. It will detect one part nickel in six million parts solution.

62. Cattelain, E., "The Use of Organometallic Complexes in Gravimetric Analysis," J. pharm. chim. (8), 2, 485-91, 525-35 (1925) [CA, 20, 1365 (1926)].

A summary of the use of diphenylglyoxime for the separation and determination of nickel and cobalt, titanium and aluminum, etc., with detailed accounts of the analytical character of each precipitate is given.

63. Ishibashi, M., "Electrolytic Reduction of Oximes. III.

Benzil Dioxime," Mem. Coll. Sci., Kyoto Imp. Univ., 8A, 383 (1925) [CA, 20, 42 (1926); J. Chem. Soc. (London), 128 (1), 1431 (1925)].

The electrolytic reduction of β -benzildioxime in ethanol-water-sulfuric acid (1.5 amp./100 cm.²) for six hours at 16-8° gives a toluylene hydrate (m.p. 61-2°, molecular weight in freezing benzene, 201), $\alpha\beta$ -diamino- $\alpha\beta$ -diphenylethane, both meso and dl forms, tetraphenylaldine, n- and isodiphenyloxyethylamine, benzoinpinacol, desoxybenzoinpinacol, n- and isohydrobenzoin. Both the α - and γ -benzildioximes behave similarly.

64. Brady, O. L., and Perry, H. M., "Methylation of the Oximes of Benzil," J. Chem. Soc. (London), 127, 2874 (1925) [CA, 20, 752 (1926)].

α -Benzildioxime and dimethyl sulfate give the N,N-dimethyl ether (m.p. 192° with decomposition). The ether crystallizes from benzene with 0.5 mole benzene (m.p. 185°) and from ethyl alcohol with 0.5 mole (m.p. 165-6°). The O,O-dimethyl ether (m.p. 163-4°) was prepared from the oxime, silver oxide, and ethyl iodide in dry ether. On heating it with concentrated hydrochloric acid, the β -derivative formed. β -Benzildioxime and dimethyl sulfate give a mixture of the N,O-dimethyl

ether (m.p. 102-3°), which is transformed by concentrated hydrochloric acid to the N-methyl ether, and the O,O-dimethyl ether (m.p. 72-3°). Methylation of the γ -dioxime gave only the N-methyl ether which suggests that the N,N- and N,O-dimethyl ethers are formed but are readily hydrolyzed.

The authors also give a discussion on the ethers prepared by others.

1927

65. Hieber, W., and Leutert, F., "Specific Action of the Oxime Group on Metallic Salts. II. Reactions of Ketoximes with Metallic Salts," Ber., 60B, 2296 (1927) [Brit. Abstr., A, 46 (1928)]7.

Two g. hexahydrate copper(II) chloride is mixed with one g. finely powdered α -benzildioxime in an alcoholic solution. After six to eight hours the precipitate is separated and recrystallized from acetone. The green copper complex is given the formula $\text{Ph-C(=NOH)-C(=NOH)-Ph.CuCl}_2$.

1928

66. Germuth, F. G., "Determination of Nickel with α -Benzildioxime in Presence of Chromium Compounds," Chemist Analyst, 17, No. 3, 7 (1928) [CA, 22, 1745 (1928)]7.

To overcome contamination of the nickel precipitate produced in the presence of chromic salt, it is recommended 0.25 g. of potassium hydrogen tartrate and 0.2 cc. of 10% copper(II) ammonium chloride solution be added. In this way correct results were obtained in the analysis of 0.25 g. nickel nitrate in the presence of 0.1 g. iron(II) nitrate and 0.1 g. chromium(III) chloride.

67. Porter, C. W., Molecular Rearrangements, Chemical Catalog Company, Inc., New York, 1928, pp. 52-53.

The author discusses the Beckmann rearrangement in relation to the three benzildioximes. The formulas that were assigned to the benzildioximes were based upon the assumption that the groups which take part in the transformation are on the same side of the molecule. From these relations we have the following: α (syn)-benzildioxime (m.p. 237°) \rightarrow dibenzylazoxime (m.p. 108°), β (anti)-benzildioxime (m.p. 206.7°) \rightarrow oxanilide (m.p. 245°), and γ (amphi)-benzildioxime (m.p. 164.6°) \rightarrow benzoylphenylurea. There has been uncertainty about the dioximes because other reactions have not always corroborated the conclusions drawn by Beckmann. For example, the γ -oxime forms a diacetyl derivative which upon saponification yields an oxime anhydride, diphenylfurazan. From this reaction it was supposed that the hydroxyl groups are in the syn-position. The syn-structure was originally assigned to the γ -oxime on this account (Hantzsch and Werner, Ber., 23, 11 (1890); Auwers and Meyer, Ber., 21, 784 (1888); A. and M., Ber., 22, 705 (1889); Beckmann and Köster, Ann., 274, 25 (1893)). The syn-formula for the γ -dioxime is also supported by the observation that diphenylglyoxime peroxide on reduction yields γ -benzildioxime (Angeli, Ber., 25, 1956 (1892)). The

structure of the peroxide is given as
$$\begin{array}{c} \text{Ph}-\text{C} \quad \text{C}-\text{Ph} \\ \parallel \quad \quad \parallel \\ \text{N}-\text{O}-\text{O}-\text{N} \end{array} ;$$

however, it has not been established with certainty (Wieland and Semper, Ann., 358, 36 (1908)). Possibilities for the structure are:

$$\begin{array}{c} \text{Ph}-\text{C} \quad \text{C}-\text{Ph} \\ \parallel \quad \quad \parallel \\ \text{N}-\text{O}-\text{N}=\text{O} \end{array} \quad \text{and}$$

$$\begin{array}{c} \text{Ph}-\text{C} \quad \text{C}-\text{Ph} \\ \parallel \quad \quad \diagup \\ \text{N}-\text{O}-\text{N} \quad \text{O} \end{array} .$$
 Another argument in favor of the

amphi-structure for γ -benzildioxime is found in the fact that through the Beckmann rearrangement the product is benzoylphenylurea.

1929

68. Meisenheimer, J., and Theilacker, W., "Constitution of Oximes. X.," Ann., 469, 128 (1929); cf. M. et al., Ann., 468, 202 (1929) [CA, 23, 3679 (1929); Brit. Abstr., A, 566 (1929)].

A reply in support of the Hantzsch-Werner view of the isomerism of oximes to Ponzio (Ber., 61B, 1316 (1928); Gazz. chim. ital., 58, 329 (1928)).

Contrary to Ponzio, the authors consider that the action of benzenediazonium chloride on α -phenylglyoxime does not involve a rearrangement (i.e., the α -glyoxime yields a nickel salt, while the resulting β -benzildioxime does not), the resulting β -benzildioxime being formed by a rearrangement of the unstable γ (amphi)-benzildioxime, which is considered the primary product because hydrolysis of its acetyl derivative yields a trace of diphenylfurazan, showing the presence of a trace of the γ -compound. Thus, the Hantzsch-Werner view in explaining some isomerism is upheld and the uncertainty of physical properties for the configuration is discussed.

69. Gutzeit, G., "A Rapid Method of Qualitative Analysis. I.

Some Specific and Special Tests For Common Cations and Anions," Helv. Chim. Acta, 12, 713 (1929) [CA, 23, 4644 (1929)]7.

α -Benzildioxime is cited as a qualitative test for nickel.

70. Hieber, W., and Leutert, F., "Reactions of Oximes With

Metallic Salts. III. Complex-Chemical Behavior of Stereoisomeric Oximes," Ber., 62B, 1839 (1929) [CA, 23, 4692 (1929)]7.

Copper(II) acetate and α -benzildioxime heated in an alcoholic, aqueous ammonium hydroxide solution yield a dark brown compound of the type $\left(\begin{array}{c} \text{Ph}-\text{C}=\text{N}-\text{OH} \\ | \\ \text{Ph}-\text{C}=\text{N}-\text{OH} \end{array} \right)_2 \text{Cu}$ (I).

An ether suspension of the α -isomer treated with hydrogen chloride and copper(II) yields the type

$\begin{array}{c} \text{Ph}-\text{C}=\text{N}-\text{OH} \\ | \\ \text{Ph}-\text{C}=\text{N}-\text{OH} \end{array} \rightarrow \text{CuCl}_2$ (II). The nickel derivative, type II,

is more stable, but can be converted to type I under anhydrous conditions. Nickel salts of the γ -isomer in

ammonium hydroxide yield $\begin{array}{c} \text{O} \\ || \\ \text{Ph}-\text{C}=\text{N}-\text{Ni} \\ | \\ \text{Ph}-\text{C}=\text{N}-\text{O} \end{array}$ (III), the oxime

acting as a dibasic acid. III is supported by the fact

that it is a compound of yellow color in contrast to the deep red nickel inner complex salt of α -benzildioxime. Copper(I) chloride converts the γ -isomer to the α - and yields an identical inner complex.

1930

71. Ponzio, G., "Dioximes. LXI.," Gazz. chim. ital., 60, 49 (1930); cf. P., Gazz. chim. ital., 59, 810 (1929) [CA, 24, 3488 (1930)]7.

α -Benzildioxime forms a complex nickel salt when an aqueous suspension is heated with nickel. The β - and γ -isomers do not give this complex. Prepared by the method of Brady and Perry (J. Chem. Soc. (London), 127, 2874 (1925)), α - and β -benzildioxime have higher melting points than those recorded by Beilstein (Vol. 7, p. 760) or by Meisenheimer and Lamparter (Ber., 57B, 276 (1924)). On crystallization from amyl alcohol rather than ethyl alcohol, the α -isomer melts at 247-8°. On crystallization from dilute ethyl alcohol containing acetic acid and a little nickel(II) acetate and then from dilute ethyl alcohol, the β -isomer melts at 211-2°. Both melting points were the same after the compounds were a year old. In the preparation of the β -form by Brady and Perry's method, a little diphenylfurazan was found in the excess of aniline. Boiling the α -isomer with a little aniline, pouring it into water containing hydrogen chloride, adding dilute sodium hydroxide, and recrystallizing the precipitate from ethyl alcohol yields diphenylfurazan (cf. Auwers and Meyer, Ber., 21, 784 (1888)). The β -isomer did not give a furazan. β -Benzildioxime may be prepared by boiling the α -isomer with aniline, pouring the mixture into dilute hydrochloric acid, and crystallizing from dilute ethyl alcohol which contains a little acetic acid and nickel(II) acetate. The α -form, fused, cooled, and treated with ethyl alcohol, leaves an undissolved substance which, after addition of acetic acid, nickel(III) acetate, and sodium hydroxide, leaves diphenylfurazan. γ -Benzildioxime heated to 170° and treated with ethyl alcohol gives the α -isomer. Some β -isomer is formed and is precipitated from the filtrate of the α -isomer. More α -compound was prepared than reported by Beckmann and Köster (Ann., 274, 1 (1893)) or by Auwers and Meyer (Ber., 22, 705 (1889)). Dilute γ -isomer precipitates the α -nickel complex when heated at 100°. The remaining

solution contains some β -isomer which precipitates on cooling. The yield of α -isomer varies from 40-70% and does not originate from the β -form. The γ -isomer is isomerized to the β -form (A. and M., Ibid.) when heated with aqueous sodium hydroxide. The β -compound also results from heating the γ -form with concentrated hydrogen chloride in a closed tube at 100°. Preparation of the α - and γ -diphenylglyoxime peroxide was attempted with sodium oxychloride. The α -form is yellow and hard to decolorize. The γ -isomer forms a compound which melts at 116-7°. The author also discusses many substituted benzildioximes.

72. Ponzio, G., "Dioximes. LXIX.," Gazz. chim. ital., 60, 825 (1930) [CA, 25, 1489 (1931)].

The present paper shows that the behavior toward hydrochloric acid in ethyl ether of the two forms of some glyoximes does not agree with the structural configurations which would be assigned to them by the theory of Hantzsch and Werner. The majority of aromatic aldoximes exist in two forms, one of which can be isomerized to the other by hydrochloric acid in ethyl ether (cf. Porter, Molecular Rearrangements, Chemical Catalog Company, Inc., New York, 1928, p. 34), whereas only a very few glyoximes have two or more forms. The present paper describes two or more cases of the latter isomerism. Though there are too few experiments on the isomerism of glyoximes to warrant any general conclusions, some authors have attempted to extend to glyoximes the distinction made by Hantzsch for monoximes, viz., that there are forms stable toward acids and forms stable toward bases. This has led to the alleged discovery of glyoxime forms which do not exist. Ponzio has already shown the insufficiency of the Hantzsch theory, and in the present paper only the experimental results of the action of hydrochloric acid on the particular glyoximes and their behavior with nickel and nickel acetate are given. They were transformed into the complex $\text{Ni}(\text{DH})_2$ (where DH is the univalent residue after removal of a hydrogen atom from an oximino group of the glyoxime DH_2), both by nickel in the presence of water and by nickel(II) ions in dilute acetic acid. In conjunction with the experiments of earlier workers, the results show that hydrochloric acid in ethyl ether isomerizes a form (1) of benzildioxime which does not give a $\text{Ni}(\text{DH})_2$ complex to a form which does give this nickel complex, (2) of chloroglyoxime which does not give a $\text{Ni}(\text{DH})_2$ complex to another form which likewise does not give the complex,

(3) of phenylglyoxime which gives a $\text{Ni}(\text{DH})_2$ complex to a form which does not give the complex, (4) of *p*-tolylglyoxime which does not give a $\text{Ni}(\text{DH})_2$ complex to a form which does give the complex, and (5) of *p*-tolylglyoxime which gives the $\text{Ni}(\text{DH})_2$ complex to a form which does not give the complex.

73. Durio, E., and Bissi, M., "Dioximes. LXXII.," Gazz. chim. ital., 60, 899 (1930) [CA, 25, 1492 (1931)].

In the oxidation of α -benzildioxime (I) with alkaline potassium ferricyanide, Auwers and Meyer (Ber., 21, 784 (1888)) obtained the diphenylglyoxime peroxide, $\text{Ph}(\text{C}_2\text{N}_2\text{O}_2)\text{Ph}$, (II) and a secondary product, $\text{C}_{28}\text{H}_{20}\text{O}_2\text{N}_2$, (III). III has never been described since, yet its formation may be of importance in explaining the dehydration of glyoximes to the so-called peroxides. The present paper shows that III is formed from the α - but not from the β -form of I, and describes the conditions which lead to a much higher yield than the extremely small yield by the procedure of Auwers and Meyer. Traces of III are also formed by the oxidation of I with NaClO (cf. Ponzio, Gazz. chim. ital., 60, 49 (1930)). Reactions of III are given and the compound proved to be dioxotetraphenylpyrazine. The formation simultaneously of II and III from I proves that potassium ferricyanide acts on I in two distinct ways: (1) simple dehydrogenation which forms II, and (2) a more complex reaction which involves the elimination as HNO_2 of two hydrogen atoms and two NOH groups from two molecules of I, thus: $2(\text{I}) + 2 \text{O} \longrightarrow (\text{III}) + 2\text{HNO}_2 + \text{H}_2\text{O}$. Since under the same conditions β - and γ -benzildioxime (IV and V) form exclusively II, both NOH groups of IV and V are dehydrogenated by oxidizing agents, whereas in I, one NOH group is dehydrogenated and the other is oxidized, i.e., toward oxidizing agents the NOH group of IV and V behave the same and those of I differently. This behavior is analogous to that with nickel(II) ions, where of the three benzildioximes only I forms the complex salt, $\text{Ni}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_2)$, by substitution of one oxime hydrogen atom.

74. Brady, O. L., and Muers, M. M., "Methylation of the Oximes of Benzil. II. The Monomethyl Ethers of the Benzil Dioximes," J. Chem. Soc. (London), 1930, 216; cf. B.

and Perry, J. Chem. Soc. (London), 127, 2874 (1925)

[CA, 24, 2455 (1930)]7.

In the following the symbols α' and β' are used to indicate the oximino group methylated in the γ -dioxime, α' being applied when the methylated HO group is vicinal and β' when it is remote from the Ph group. O-Methyl- α -benzilmonoxime on oximation gives a mixture of O-monomethyl- α -benzildioxime (I), m.p. 181-2° (acetyl derivative, m.p. 107-8°; benzoyl derivative, m.p. 167°) and α' -O-monomethyl- γ -benzildioxime (II), m.p. 172° (acetyl derivative, m.p. 80°; benzoyl derivative, m.p. 79°). The final yields averaged 40-50% of the α - and 7-10% of the γ -benzildioxime derivatives with about 25% of inseparable mixture. O-Methyl- β -benzilmonoxime does not react readily with hydroxylamine, it being necessary to heat it to 175-85° with hydroxylamine hydrochloride in ethanol; the only product formed is O-monomethyl- β -benzildioxime (III), m.p. 177° (acetyl derivative, m.p. 81°; benzoyl derivative, m.p. 162°). α -Benzildioxime on monomethylation gives a mixture of I and N-monomethyl- α -benzildioxime (IV), m.p. 168°; β -benzildioxime gives III and N-monomethyl- β -benzildioxime (V), m.p. 205° (decomposition); the γ -dioxime gives only V. Methylation of I gives a mixture of the O,O- and O,N-di-Me derivatives; IV gives the same compounds. Methylation of III gives a mixture of O,N- and O,O-di-Me derivatives; II gives the O,O-dimethyl- α -benzildioxime and O,O-dimethyl- γ -benzildioxime, m.p. 59°. I (20 g.) in aniline (40 cc.), heated to boiling for 30 seconds and poured into ice-cold dilute hydrochloric acid, gives 5 g. of II; if the time of contact is longer than 30 seconds, a larger quantity of III is formed, which is very difficult to separate. When 4 g. I is boiled five minutes with 10 cc. aniline, 2 g. III results. A suspension of 8 g. I in glacial acetic acid, saturated with dry hydrochloric acid and boiled for 30 minutes, gives 5 g. III. Other isomeric changes are discussed. I and phosphorus pentachloride in dry ether give a mixture of 3,5-diphenyl-1,2,4-oxadiazole and N-benzoyl-O-methylbenzamidoxime, m.p. 151°. Beckmann rearrangement of II gives α -O-methylphenylglyoxylanilideoxime, m.p. 118-20°; III gives the corresponding β -derivative, m.p. 152°; boiling concentrated hydrochloric acid converts it into the α -isomer. The β -derivative was synthesized by the action of methyl iodide and silver oxide upon β -phenylglyoxylanilideoxime.

75. Germuth, F. G., "Study of Various Methods for the Separation and Estimation of Nickel and Cobalt Salts," Chemist Analyst, 19, No. 2, 4 (1930) [CA, 24, 1819 (1930)].

Three methods for determining nickel in the presence of cobalt and one for the determination of cobalt in the presence of nickel were studied and excellent results obtained with each. For the determination of very small quantities of nickel, the α -benzildioxime method is recommended but the results with diacetyldioxime are as good when not more than 0.1 g. of cobalt is present.

76. Englund, B., "Reaction Between Polyatomic Alcohols or Phenols and Arsenic Compounds, Especially Arsonacetic Acid," J. prakt. Chem. (2), 124, 191 (1930); cf. E., J. prakt. Chem. (2), 122, 121 (1929) [CA, 24, 1841 (1930)].

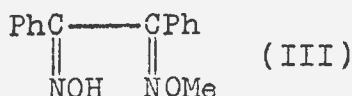
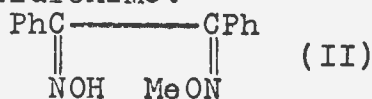
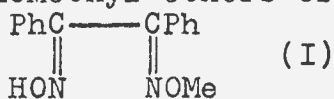
The solubility of arsenic compounds was studied in diol solutions. The following values of L (the increase in solubility of the arsenic compound per diol concentration) for β - and γ -benzildioxime were given as 0.016 and 0.037, respectively.

77. Grisolle, H., and Servigne, M., "Principal Organic Reagents Used in Inorganic Chemistry," Ann. chim. anal. chim. appl., 12, 321 (1930) [CA, 25, 261 (1931)].

The uses of cupferron, benzidine, dicyandiamidine, nitron, dimethylglyoxime, sodium nitroso-2,3,6-naphtholdisulfonate, α -benzildioxime, benzoylmethylglyoxime, α -furildioxime, and oxalenediuramidoxime, $(\text{NH}_2\text{CONHC}(\text{:NOH}))_2$, are outlined in this installment of a carefully prepared paper.

78. Brady, O. L., and Muers, M. M., "Coordination Compounds of Oximes," J. Chem. Soc. (London), 1930, 1599 [CA, 24, 5296 (1930)].

The formulation of the metallic complexes of oximes still presents difficulties and in the hope of throwing more light on this subject it was proposed to study the complex formation of the four possible O-monomethyl ethers of benzildioxime:



Only the first three have been prepared (B. and M., J. Chem. Soc. (London), 1930, 216). Only I gave complexes, which are the type R_3Co and R_2Ni . Various formulas are proposed for these complexes. The cobalt complex of I, red-brown, m.p. $165-9^\circ$ (decomposition), is obtained from 5 g. I in 60 cc. boiling acetone and 3 g. cobalt(III) nitrate in a little water, and then adding 10 cc. 2 N ammonium hydroxide and pouring into excess of 0.1 N sodium hydroxide. With cobalt(III) acetate some complex is formed before the addition of ammonium hydroxide but the yield is not so good. Sodium hydroxide may be used in place of ammonium hydroxide, indicating that ammonia plays no essential part in the complex formation. The production of the complex depends on the presence of atomic oxygen. The complex could not be crystallized. The nickel complex of I is a brown powder, cannot be crystallized, and is difficult to obtain pure; with potassium cyanide I is regenerated. Copper and iron(II) complexes of I are so unstable that they cannot be isolated. The cobalt complex of α -benzildioxime, brown, forms from the oxime and cobalt(III) acetate. γ -Benzildioxime yields a mixture of cobalt complexes, which could not be purified.

1931

79. Milone, M., "Dioximes. LXXIX.," Gazz. chim. ital., 61, 584 (1931) [CA, 26, 711 (1932)].

The work, which was suggested by the lack of data on the rate of hydrolysis of oximes (cf. Auwers and Siegfeld, Ber., 26, 788 (1893); Meisenheimer and Lamparter, Ber., 57B, 276 (1924)), begins a study, from the kinetic point of view, of the hydrolysis of acyl derivatives of various forms of symmetrical and asymmetrical glyoximes, with a view to determining the

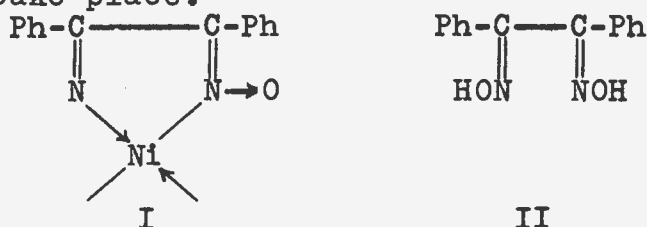
relations between structure and tendency to hydrolyze. The compounds were hydrolyzed with sodium carbonate and sodium bicarbonate in 60% ethanol, at 25°, in a 0.01 M concentration (diacetyl and dibenzoyl derivatives, 3.24 and 4.48 g., respectively, per l.). The solutions were titrated periodically with 0.01 N hydrochloric acid (phenolphthalein). By assuming that the reaction takes place in two steps, (1) diacetyl derivative \longrightarrow monoacetyl derivative and (2) monoacetyl derivative \longrightarrow glyoxime, and that at the beginning (1) predominated and toward the end (2) predominated (cf. Knoblauch, Z. physik. Chem., 26, 96 (1898)), the hydrolysis is simple and the two constants K_m and K_{ac} can be calculated, adopting for a values corresponding at first to the molar concentrations of the diacetyl derivative, then double a values (corresponding to N concentrations with respect to the NOH groups), and applying the general formula: $du/dt = k(a - u)(b - u)/(c + u)$, which gives $k = \{1/\sqrt{(t_2 - t_1)(b - a)}\} \{ (a + c) \log \sqrt{(a - u_1)/(a - u_2)} - (b + c) \log \sqrt{(b - u_1)/(b - u_2)} \}$, where u is the quantity of diacetyl derivative hydrolyzed in time t. The concentrations of sodium carbonate and sodium bicarbonate must be varied so that the reaction does not proceed too slowly or too rapidly. The following data give the experimental k_1 , k_2 , and $n(k_1/k_2)$ values of the six compounds:

α -PhC(:NOAc)C(:NOAc)Ph (I) (cf. A. and S., loc. cit.), 18×10^{-2} , 3×10^{-3} , 56; β -PhC(:NOAc)C(:NOAc)Ph (II) (cf. A. and S., Ibid.), 2.5×10^{-2} , 5×10^{-4} , 50; γ -PhC(:NOAc)C(:NOAc)Ph (III) (cf. A. and S., Ibid.), 7×10^{-2} , 1.5×10^{-3} , 47; α -PhC(:NOBz)C(:NOBz)Ph (IV) (M. and L., loc. cit.), 6×10^{-2} , 9×10^{-3} , 6; β -PhC(:NOBz)C(:NOBz)Ph (V) (M. and L., Ibid.), 1×10^{-2} , 4×10^{-4} , 25; γ -PhC(:NOBz)C(:NOBz)Ph (VI) (M. and L., Ibid.), 2.5×10^{-2} , 4×10^{-3} , 6. I and IV hydrolyze about six times as fast as do II and V, and about three times as fast as III and VI. With II and VI, however, the reaction is complicated by the fact that under the conditions the α -PhC(:NOH)C(:NOH)Ph is transformed by loss of water into diphenylfurazan, and because such a disappearance increases the velocity of hydrolysis, it is probable that the values for III and VI are doubtful. The experiments do not allow any general conclusions, particularly because in a symmetrical glyoxime the two lateral chains exert an equal influence on the C(:NOH)C(:NOH) group. It is not even possible to compare the experimental values and the structure of the three benzildioximes.

1933

80. Taylor, J., and Sutton, L., "The Configuration of Aldoximes From Measurement of Electrical Dipole Moment," J. Chem. Soc. (London), 1933, 63 [CA, 27, 1626 (1933)].

Evidence that there is no change in configuration when an oxime is metholated is afforded by Brady and Muers (J. Chem. Soc. (London), 1930, 216, 1599) on the properties of the methyl ethers of benzildioxime. It is now established that in the nickel derivative, R_2Ni , of α -benzildioxime the attachment of the dioxime residue to the nickel is as shown in I (Hieber and Leutert, Ber., 62B, 1839 (1929)) and that such a derivative is formed by the α -isomer and not by the β -isomer because the former has the structure II in which the space arrangement is already suitable for such attachment to take place.



Brady and Muers found that the O-monomethyl ether of α -benzildioxime gave an ether which is still capable of forming complexes R_2Ni and R_3Co . Hence, it seems clear that the configuration of the O-ether compounds corresponds to that of the parent oxime.

81. Meisenheimer, J., and Dorner, O., "Absorption Spectra of Oximes," Ann., 502, 156 (1933) [CA, 27, 3194 (1933)].

Absorption curves are given for the α -, β -, and γ -benzildioximes. The solutions were made up in ethanol, 10% potassium hydroxide, and pyridine. The relation of absorption spectra, stability, and constitution is discussed.

82. Milone, M., "Dioximes. CI.," Gazz. chim. ital., 63, 744 (1933) [CA, 28, 2713(1) (1934)].

Ultraviolet radiation (Gallois mercury-vapor lamp, 4000 candle power, 50 cm. distance) isomerizes the

α - and γ -form of certain glyoximes, both in the solid state and diluted in ethanol, at 18° to the β -forms, from which the nickel salts can be obtained. The isomerization is also promoted by sunlight but very slowly, and is more rapid in 30-40% ethanol than in the solid state. α -Benzildioxime exposed 26 hours and dissolved in ethanol gave 29% of the β -isomer; γ -benzildioxime under similar conditions gave 41% of the more stable β -compound. In the solid state α -benzildioxime gave 15.9% while the γ -isomer gave slightly more, 22.4%.

83. Cambi, L., and Cagnasso, A., "The Structure and Magnetic Susceptibility of Complex Ferrous Compounds," Gazz. chim. ital., 63, 767 (1933) [CA, 28, 3329(8) (1934)].

The complex ferrous derivatives of the glyoximes, prepared by the method of Chugaev, include the dimethyl derivative, $(C_4H_7O_2N_2)_2Fe \cdot 1.5C_5H_5N$, already known, and the diphenylglyoxime, $(C_{14}H_{11}O_2N_2)_2Fe \cdot 3.5C_5H_5N$. The magnetic susceptibilities of all the compounds studied at various temperatures are tabulated. In conjunction with earlier investigations (C. and C., Atti reale accad. Lincei, 13, 809 (1931); Cambi, Atti soc. ital. progr. sci., 20 (1), 509 (1932)), the results show that compounds with a -N:C:C:N- chain form ferrous complexes in which the diamagnetic forms predominate, which seems to be related to the polar symmetry of the ring in the complex. Compounds with a non-symmetrical -N:C:C:O- chain form complexes in which the paramagnetic form predominates up to the maximum susceptibility of the ferrous ion. The structure and polar dissymmetry is probably governed by the electronic configuration of the complex.

1934

84. Milone, M., "The Electric Moments of Dioximes. I.," Congr. intern. quim. pura y apl. 9th Congr., Madrid, 2, 191 (1934) [CA, 29, 7139(9) (1935)].

The structure of oximes can be obtained from the following measurements on various concentrations of their solutions in dioxane (b.p. 100.7°, d_4^{20} 1.0340, n_D^{20} 1.4224, ϵ_{20} 2.295): density, refractive index, dielectric constant, polarization of solution, solvent

and solute (extrapolated to zero concentration), molar refraction, and electrical moment. The electrical moments ($\times 10^{-18}$ esu) for α -, β -, and γ -benzildioxime (m.p. 214° , 244° , and 165°) are given as 1.492, 2.12, and 1.55.

1935

85. Durio, E., "Dioximes. CVI.," Gazz. chim. ital., 65, 89

(1935) [CA, 29, 4737(7) (1935)]_7.

Both α - and β -benzildioxime react with phenylhydrazine to give the osazones. In the case of the osazones, the α -form has the syn-configuration because by elimination of aniline it gives triphenylosotriazole and by dehydration it gives tetraphenylosotetrazine. The β -form has the anti-configuration. These conclusions are in agreement with the fact that the osazones give only one monoacetyl derivative.

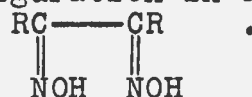
86. Milone, M., "Dioximes. CVII.," Gazz. chim. ital., 65, 94

(1935) [CA, 29, 4738(5) (1935)]_7.

The experiments are a continuation of similar experiments by Sutton and Taylor (J. Chem. Soc. (London), 1931, 2190; Ibid., 1933, 63) and Parsons and Porter (J. Am. Chem. Soc., 55, 4745 (1933)) and are the first measurements of the molecular electric moments of dioximes, specifically glyoximes. The apparatus, which is described in detail, was of a special heterodyne type, but was similar to that of Smyth (J. Am. Chem. Soc., 50, 1536 (1928)) and Wolf (Z. physik. Chem., 14, 305 (1931)). Dioxane solutions of the compounds were utilized.

The molecular electrical moments divided by 10^{-18} for α -, β -, and γ -benzildioxime are given as 1.492, 2.12, and 1.55. The results show that (1) all forms of glyoximes have molecular electric moments, (2) when a glyoxime has more than one form, the β -form always has a greater moment than do the other forms, and (3) symmetrical alkylglyoximes have greater moments than do their next asymmetrical homologs. Because there is a symmetrical RCCR group in symmetrical dialkylglyoximes, the moment should be the vectorial sum of the partial moments of the two NOH groups, and because the moment is not zero, it is logical to assume that the two NOH

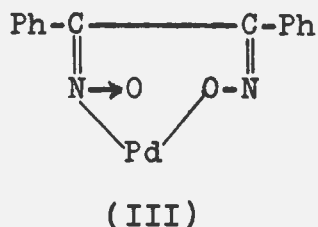
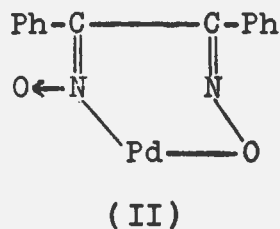
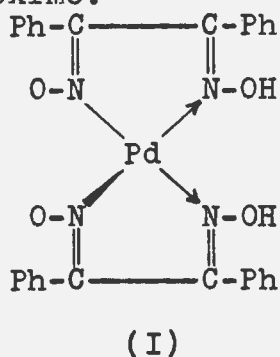
groups are located in symmetrical positions with respect to the center of the configuration which represents in a plane the arrangement and direction of the atomic groups. The only configuration in accord with these facts is the amphi:



In an analogous way, the forms of arylglyoximes with the greater moments have amphi-configurations, in fact, only in amphi-configurations can the vectorial sum of the partial electric moments of the NOH groups be other than zero. Based on the experimental moments, therefore, the β -forms of the glyoximes must have amphi-configurations, i.e., the forms which give a nickel salt of the $(\text{DH})_2\text{Ni}$ type. The difference between the moments of the two forms of a glyoxime is small, and is in all cases smaller than would exist if there were a change in the sign of the partial electric moment of the NOH groups, in conformity with the stereochemical hypothesis, and as was observed by Sutton and Taylor for nitrooximes.

87. Dwyer, F. P., and Mellor, D. P., "Compounds of Palladium with Benzil Dioxime," J. Proc. Roy. Soc. N. S. Wales, 68, 107 (1935) [CA, 29, 4690(6) (1935)].

Compounds of palladium with α -, β -, and γ -benzildioxime were prepared to determine which of the three forms yield 4-covalent inner complexes with palladium. Palladium like nickel forms a compound (I) in which two molecules of dioxime are coordinated with the metal only in the case of the α - or anti-benzildioxime.



This compound was prepared by the addition of a boiling alcoholic solution of the dioxime to a boiling neutral solution of sodium chloropalladite. An alternate method consists in boiling palladium γ -benzildioxime with an excess of α -benzildioxime in acetone solution and removing the excess α -dioxime and the displaced γ -dioxime by treating with dilute sodium hydroxide. Like nickel, palladium also forms with the γ - or amphi-dioxime an orange-yellow compound (II) in which only one molecule of dioxime is combined with palladium. II was prepared by the addition of a cold alcoholic solution of γ -benzildioxime to a solution of sodium chloropalladite and sodium acetate. No other compound of palladium with the γ -dioxime could be prepared.

Unlike all other metals, palladium in neutral and acid solutions coordinates with the β - or syn-form of dioxime to form compound (III), prepared in a manner analogous to that for II. Because of its high specificity β -benzildioxime may be used as an analytical reagent for the determination of palladium. Three γ /cc. of palladium can be detected.

88. Malaviya, B. K., and Dutt, S., "Photoreaction in Tropical Sunlight," Proc. Acad. Sci., United Provinces Agra and Oudh, India, 4, 319 (1935) [CA, 30, 1056(7) (1936)].

The action of strong sunlight on a large number of organic compounds was studied. Solutions, usually 2%, in water, dilute hydrochloric acid, dilute sodium hydroxide, or ethanol, made from carefully purified compounds, were exposed to full sunlight until it was seen that no action was to occur. α -Benzildioxime in dilute sodium hydroxide gave 3,4-diphenylfurazan, m.p. 94°. This was for a time of 35 days exposure.

1936

89. Mironoff, J., "Oxidimetric Determination of the Oximes of Nickel and Copper," Bull. soc. chim. Belg., 45, 1 (1936) [CA, 30, 6672(7) (1936)].

The volumetric method described by Tougarinoff (Ann. soc. sci. Bruxelles, 54B, 314 (1934)) gives quantitative results when small amounts of copper and nickel are precipitated with phenylglyoxime (I),

diacetylmonoxime (II), diphenylglyoxime (III), or benzoinoxime (IV). The same procedure as that used with dimethylglyoxime can be used for I and II, but with III hydrolysis must be performed carefully on account of frothing. With IV the benzoin formed must be removed or high results are obtained.

90. Cambi, L., and Coriselli, C., "Cobalt Salts of Glyoximes.

II. Cobaltic, Diglyoximic and Sesquiglyoximic Salts,"

Gazz. chim. ital., 66, 91 (1936) [CA, 30, 8160(1) (1936)].

Cobalt(II) acetate and α -benzildioxime form the insoluble compound Co_2Df_3 and the soluble compound DfHCoDf . Co_2Df_3 and hydrogen bromide form the compound $[(\text{DfH})_2\text{CoBr}_2]\text{H}$. The glyoximes studied differ from isonitroketones and isonitroso- β -naphthol in that these latter form internal complexes with octahedral structure, whereas the glyoxime salts contain only a univalent radical. The glyoxime residues exclude the external trisalt structure, or at least render it unstable. For convenience α -benzildioxime is abbreviated DfH_2 . Various other salts are discussed by the authors.

91. Milone, M., "X-ray Study of the Structure of Some Bibenzyl Derivatives," Z. Krist., 93, 113 (1936) (in English)

[CA, 30, 6260(4) (1936)].

α -Diphenylglyoxime, $\text{C}_6\text{H}_5.\text{C}(:\text{NOH}).\text{C}(:\text{NOH})\text{C}_6\text{H}_5$, is monoclinic, with $a = 25.08 \text{ \AA}$, $b = 8.68 \text{ \AA}$, $c = 11.92 \text{ \AA}$, $\beta = 120^\circ 50'$; $Z = 8$, space group $\text{C}_{2h}^2\text{-C2/c}$; $d. = 1.336$, calculated $d. = 1.416$. Diphenylglyoxime peroxide, $\text{C}_6\text{H}_5.(\text{C}_2\text{N}_2\text{O}_2).\text{C}_6\text{H}_5$, also monoclinic, $a = 12.85 \text{ \AA}$, $b = 6.27 \text{ \AA}$, $c = 14.96 \text{ \AA}$, $\beta = 116^\circ 50'$; $Z = 4$, space group $\text{C}_{2h}^2\text{-P2}_1/\text{c}$; $d. = 1.353$, calculated $d. = 1.430$. Diphenylfurazan, $\text{C}_6\text{H}_5.(\text{C}_2\text{N}_2\text{O}).\text{C}_6\text{H}_5$, is orthorhombic, $a = 11.89 \text{ \AA}$, $b = 12.95 \text{ \AA}$, $c = 6.99 \text{ \AA}$; $Z = 4$, space group $\text{D}_2^2\text{-P2}_12_12_1$, (a slight but definite pyroelectric effect was observed); $d. = 1.312$, calculated $d. = 1.361$.

92. Ponzio, G., "Dioximes. CX.," Gazz. chim. ital., 66, 119 (1936) [CA, 30, 8194(6) (1936)]_7.

α -Phenylglyoxime peroxide and PhMgBr form α -diphenylglyoxime, $\alpha\text{-PhC}(\text{:NOH})\text{C}(\text{:NOH})\text{Ph}$ (isolated by means of its cupric salt), m.p. $206-7^\circ$.

93. Milone, M., and Venturello, G., "Molecular Heats of Combustion," Atti accad. sci. Torino. Classe sci. fis., mat. e nat., 71, 395 (1936) [CA, 31, 312(8) (1937)]_7.

Heats of combustion of the aliphatic and aromatic series of glyoximes were determined. By studying the results of the different series and the fact that the difference in the heat of combustion of the three isomers of benzildioxime was different by a small amount, the conclusion was that the three isomers of benzildioxime were geometric isomers.

94. Milone, M., and Venturello, G., "Dioximes. CXVIII.," Gazz. chim. ital., 66, 808 (1936); cf. M., Gazz. chim. ital., 65, 94 (1935) [CA, 31, 4646(9) (1937)]_7.

Thermal measurements of two series of glyoximes, (1) aliphatic glyoximes existing in only one form (nickel salts of the $(\text{DH})_2\text{Ni}$ type) and (2) aromatic glyoximes existing in two or more forms, were made with a view to determining whether the assertions of Fajans (cf. Ber., 53B, 643 (1920); Z. physik. Chem., 79, 395 (1921)) and Freudenberg (Stereochemie, Leipzig, 1933, p. 739) on the nonreciprocal influence of bonds between adjacent atoms are of general application. The data were compared with the heats of combustion of a few monoöximes (cf. Landrieu, Compt. rend., 140, 867 (1905); Valeur, Ann. chim. et phys. (7), 21, 470 (1900); Swietoslawski, J. Am. Chem. Soc., 42, 1092 (1920)), which are the only previous determinations on this type of compounds. Here the method of Lemoult (Ann. chim. et phys. (8), 1, 496 (1904); J. chim. phys., 11, 805 (1913)) was used for the recalculations, for by this method heats of combustion of functional groups (thermochemical modulus) can be obtained. Since the data on monoöximes gave a modulus of approximately 70 calories for the NOH group, it was to be expected that

the two groups in the compounds of the present work would show a modulus of approximately 140 calories. The following data give the molecular heat of combustion (in calories), and the thermochemical modulus of the NOH group for each of the compounds studied:

HC(:NOH)C(:NOH)H, 304.2, 147.2; MeC(:NOH)C(:NOH)H, 457.8, 143.8; MeC(:NOH)C(:NOH)Me, 607.8, 126.8; α -PhC(:NOH)C(:NOH)H (I), 1022.2, 143.2; β -PhC(:NOH)C(:NOH)H (II), 1037.2, 159.2; α -p-MeC₆H₄C(:NOH)C(:NOH)H (III), 1177.6, 141.6; β -p-MeC₆H₄C(:NOH)C(:NOH)H (IV), 1193.8, 157.8; α -PhC(:NOH)C(:NOH)Ph (V), 1737.4, 136.4; β -PhC(:NOH)C(:NOH)Ph (VI), 1731.8, 130.8; γ -PhC(:NOH)C(:NOH)Ph (VII), 1740.2, 139.2. These results show that (1) two NOH groups, even in homologs of chemically similar forms, do not show the same thermochemical moduli, i.e., the latter varies from 130.8 to 158 calories; (2) the thermochemical moduli of the NOH groups in aliphatic β -glyoximes diminish as the homologous series progresses; (3) where a glyoxime exists in isomeric forms, the modulus of the NOH group in the β -compound is always greater than that of the other forms; (4) considerable differences exist between the heats of combustion of I and II, and of III and IV; relatively small differences between V, VI, and VII. Based on calorimetric data, V, VI, and VII may be regarded as geometric isomers (with differing relative spatial arrangement of the two NOH groups), whereas I and II and III and IV, respectively, are structural isomers. The differences in the thermochemical moduli of the NOH groups in a homologous series indicate that the structure of the entire molecule, i.e., the arrangement of the various atomic groups, has a preponderant influence on the physical properties of the various forms.

1939

95. Cambi, L., and Malatesta, L., "Cobalt Salts of Glyoximes. V.," Gazz. chim. ital., 69, 547 (1939); cf. Cambi and Coriselli, Gazz. chim. ital., 66, 91 (1936); C. and C., Rend. ist. lombardo sci. Pt. I., 71, 327 (1938) [CA, 34, 1579(7) (1940)]_7.

The cobalt complex was prepared by letting 48 g. of α -diphenylglyoxime in absolute ethyl alcohol and

22 g. of cobalt(II) bromide stand at 60° until crystallization is complete. Fifty cc. of fuming hydrobromic acid was added and refluxed for one hour. The product was fractionally crystallized from chloroform and black crystals with the formula $\left[\text{Co}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_2)_2\text{Br}_2 \right] \text{H}$, which became green upon pulverization, resulted. The magnetic susceptibility of this compound was reported as $X_M = -320 \times 10^{-6}$, $X_A = 26 \times 10^{-6}$. The mother liquor was found to yield less brominated compounds with ill-defined cobalt:glyoxime ratios (less than 1:2). Ten g. of the cobalt-diphenylglyoxime complex in 100 cc. of absolute ethanol and 20 g. potassium acetate, refluxed for 15 minutes was found to yield the hydrate $\left[\text{Co}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_2)_2(\text{OH})_2 \right] \text{H} \cdot \text{H}_2\text{O}$ which was a maroon red color. Its magnetic susceptibility was reported as $X_M = 208 \times 10^{-6}$, $X_A = 104 \times 10^{-6}$ measured at 18°. When heated to 120° in vacuo over phosphorus pentoxide the hydrate is found to lose one mole of water. Above 120° it loses water more rapidly.

Direct precipitation of the anhydrous salt was impossible because of the insolubility of α -diphenylglyoxime. However, if a mixture of the cobalt- α -diphenylglyoxime is refluxed with cobalt(II) acetate in anhydrous acetone the black anhydrous cobalt(II) salt $\left[\text{Co}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_2)_2 \right]$ is precipitated. Its magnetic susceptibility is $X_A = 1740 \times 10^{-6}$, $X_M = 1512 \times 10^{-6}$. The cobalt(III) salt $\left[\text{Co}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_2)_2\text{OH} \right]$ remains in solution and may be precipitated by the addition of water. This salt is dehydrated at 120° in vacuo over phosphorus pentoxide to the cobalt(III) salt $\left[\text{Co}(\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2)\text{H} \right]$ with the magnetic susceptibility of $X_M = -251 \times 10^{-6}$, $X_A = 30 \times 10^{-6}$.

1940

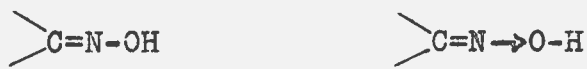
96. Peshkova, V. M., "Determination of Small Amounts of Nickel in the Presence of Other Metals," Zavodskaya Lab., 9, 407 (1940); cf. P., Zavodskaya Lab., 8, 921 (1939) [CA, 34, 7208(5) (1940)].

Various methods for the determination of nickel in the presence of copper, iron, chromium, aluminum, or cobalt were tested. The reaction with α -benzylidioxime is somewhat more sensitive than that with dimethylglyoxime and there is less danger of the formation of an impure precipitate when an alcoholic solution of the reagent is used.

97. Diehl, H., The Applications of the Dioximes to Analytical Chemistry, G. Frederick Smith Chemical Co., Columbus, Ohio, (1940) CA, 35, 1728(7) (1941) 7.

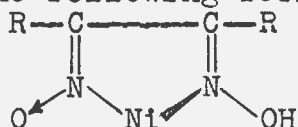
The author points out that the metal dioxime complexes exist in the form of chelate rings and that the complexes are non polar, soluble in non-ionizing solvents, have low m.p. and b.p., sublime readily, are relatively stable, and are colored.

Historically, the author states that Meisenheimer indicated that the configuration of the α -form was anti. Preiffer correlated this with the two tautomeric forms proposed by Brady and Metha.



oxime nitro

and proposed the following formulation:



Pfeiffer obtained evidence of this formulation by work with the copper and nickel salts of α -benzildioxime.

The nickel derivative of α -benzildioxime was described by Tschugaëff and first applied to analysis of nickel by Attack. α -Benzildioxime was synthesized by dissolving 10 g. of benzil in 50 ml. of methanol containing 8 g. of hydroxylamine hydrochloride and boiling for three hours. The dioxime was filtered and washed with hot water and a small amount of 50% ethyl alcohol. The purity of the product was determined by its melting point.

In the gravimetric determination of nickel it was reported that 25 mg. of the complex precipitated from an ammoniacal solution is the optimum amount for the determination. A possibility of slight contamination of the precipitate is recognized and it is recommended that the precipitate be ignited to the oxide for accurate work.

The sensitivity of the test for nickel and the action of interfering elements were reported. A reagent solution of 0.05% in alcohol with 5% ammonium hydroxide was used. An immediate precipitate of the complex was formed in the presence of nickel of a concentration of one part in 2,000,000 in the absence of interfering cations or of nitrate. In the presence of 100 times as much cobalt as nickel the complex was formed in an ammoniacal solution if the nickel

concentration was one part in 1,000,000. In the presence of larger amounts of cobalt, the cobalt is first oxidized. It was found that α -benzildioxime gave a purple color with ferrous iron which did not mask the nickel reaction. Citrate or tartrate may be added to complex the iron and will prevent its coprecipitation when iron is present in 1000 times the concentration of nickel. Silver, magnesium, chromium, zinc, or manganese did not interfere in the reaction.

The nickel α -benzildioxime complex was reported to be red in color, insoluble in neutral and ammoniacal solutions, and insoluble in mineral acids and cyanide solutions. The nickel complex with α -benzildioxime was found to be less soluble than the dimethylglyoxime complex. A palladium complex was formed which apparently decomposed rapidly.

1941

98. Diehl, H., "Dimethylglyoxime and the General Use of Organic Precipitants in Inorganic Analysis," ASTM Bull., No. 108, 28 (1941) [CA, 35, 2807(9) (1941)] 7.

Particular attention is paid to the use of dimethylglyoxime (Tschugaeff, Z. anorg. Chem., 46, 144 (1905)), cupferron (Baudisch, Chemiker-Ztg., 33, 1298 (1909)), γ -hydroxyquinoline (Berg, Z. anal. Chem., 72, 177 (1927)), α -benzildioxime (Atack, Chemiker-Ztg., 37, 773 (1913)), and dithizone (Fischer, Z. angew. Chem., 42, 1025 (1929)). Bibliography of twelve titles.

99. Wengert, P., Duckert, R., and Busset, M.-L., "Critical Study of Qualitative Reagents for the Cations. Reagents for Nickel," Helv. Chim. Acta, 24, 889 (1941); cf. W., D., and B., Ibid., 657 [CA, 36, 2225(3) (1942)] 7.

Of approximately 100 reagents tested the following are recommended: For tests under the microscope: potassium dichromate + pyridine, dimethylglyoxime, and dicyanodiamidine + potassium hydroxide. Spot plate tests: dimethylglyoxime, o-cyclohexanedionedioxime, α -furildioxime, dithioxamide, and biacetylmonoxime. Spot tests on filter paper: dimethylglyoxime, o-cyclohexanedionedioxime, and dithioxamide. Test tube

reactions: sodium bicarbonate + oxidizing agents (hydrogen peroxide, bromine), dimethylglyoxime, diphenylglyoxime, o-cyclohexanedionedioxime, α -furildioxime, dithioamide, biacetylmonoxime, and formaldoxime + potassium hydroxide. Electrographic printing: benzidine and sodium sulfide. The bibliography, characteristics of the test, sensitivity, and specificity are given.

1947

100. Tribalat, S., "Determination of Rhenium with α -Benzil Dioxime," Compt. rend., 224, 469 (1947) [CA, 41, 3397b (1947)]; Brit. Abstr., C., 125 (1948) 7.

Septivalent rhenium in the presence of dimethylglyoxime and tin(II) chloride gives a yellow complex (cf. Tougarinov, Bull. soc. chim. Belges, 43, 111 (1934)). Similarly with α -benzildioxime in warm, 9-18 N sulfuric acid a colored compound is obtained which can be extracted with amyl alcohol, iso-amyl alcohol, and the corresponding acetates. The valence of rhenium in this complex is probably higher than 4 and lower than 7. It is recommended the solution be made 12 N in sulfuric acid and 0.5-1.00 ml. used for the analysis. Add 1-2 mg. of pure α -benzildioxime, 0.5 ml. of iso-amyl alcohol, and 4 drops of freshly prepared 15% tin(II) chloride solution in 9 N sulfuric acid. Heat near the boiling point for three minutes. The solution turns yellow, then pink or red according to the rhenium content. Add 1 ml. of water; the amyl alcohol layer will contain all the rhenium. From 0.2-0.5 γ of rhenium can be detected. A blank should be run when the rhenium content is low. If more than ten times as much molybdenum is present as rhenium, it is necessary to reduce molybdenum(VI) with tin(II) chloride under conditions which prevent the reduction of rhenium(VII). It is possible to detect 5 γ of rhenium in the presence of 5 mg. of molybdenum by first reducing in 9 N sulfuric acid so that a brown (not blue) molybdenum color is obtained. Then add the dioxime reagent and test for rhenium in 16 N sulfuric acid. Finally dilute with twice as much aqua regia; the rhenium compound will all pass into the amyl alcohol layer.

1948

101. Fry, S. S., "Selenium Rectifier," U.S. 2,446,465-8, March 8, 1948 [Brit. Abstr., B., 886 (1949)]

The blocking layer is formed by subjecting the selenium surface to α -benzildioxime vapors.

102. Cohen, S. G., and Sparrow, D. B., "Action of Regulators in Polymerization of Monomers Containing Allyl and Methacrylate Groups," J. Polymer Sci., 3, 693 (1948) [CA, 43, 8199c (1949)]

The effect of α -benzildioxime on the polymerization of allyl methylacrylate was examined. It was found to have no effect on the time or extent of the formation of the insoluble gel whose formation is the first step in the reaction.

1949

103. Tsumaki, T., and Yamaguchi, M., "Pyrolysis of Inner Complex Salts," J. Chem. Soc. Japan, Pure Chem. Sect., 70, 10 (1949) [CA, 45, 4657b (1951)]

The pyrolysis of nickel dimethylglyoxime, nickel benzildioxime, nickel cyclohexanedionedioxime, and nickel α -furildioxime was studied in an atmosphere of nitrogen. The nickel salt of benzildioxime decomposed slowly at 280° giving ammonia, phenyl cyanide, diphenylfurazan, benzoic acid, and unidentified white crystals, m.p. 238°.

104. Feigl, F., and Feigl, H. E., "On the Reactivity of Inner Complex-bonded Palladium. A New Specific Test for Cyanides in Alkaline Solutions," Anal. Chim. Acta, 3, 300 (1949) (in English) [CA, 43, 8956a (1949)]

The inner-complex salts of palladium with dimethylglyoxime, benzildioxime, furildioxime, salicylalldoxime, and 8-hydroxyquinoline do not enter into oxidation-reduction reaction with carbon monoxide, either in the solid or the molecularly dispersed states. Solutions of palladium dimethylglyoxime or salicylalldoxime in alkaline hydroxide or ammonia solution are masked with respect to many reactions of both palladium and the organic component, but demasking occurs when alkaline cyanides are added. This permits a new sensitive test for cyanide ions, suitable for the detection in illuminating gas, which can be carried out directly in alkaline solution. Identification limit: 0.2 γ of cyanide; dilution limit: 1:250,000. The mechanisms of the dissolution and demasking processes are discussed.

105. Hjarles, S. R., "Synthesis of α -Benzyldioxime and Its Application in the Determination of Nickel," Actas y trabajos Congr. peruano quím., 3rd Congr., 2, 461 (1949) [CA, 46, 9465a (1952)].

The preparation of α -benzyldioxime from benzil and hydroxylamine-hydrochloride is described and its use as a test for nickel is discussed.

1950

106. Ākač, A., and Šimek, M., "Salts of Hydroxy Oximes," Collection Czechoslov. Chem. Commun., 15, 445 (1950) (in English) [CA, 45, 8979g (1951)].

The change of linkage to carbonyl oxygen alters the properties of the salts so that they have a constitution quite different from the salts of the corresponding dioximes. Several nickel salts of oximes are given. A nickel salt of γ -benzildioxime is cited as an other precipitate which is assumed to have a metal-oxygen linkage. This precipitate is quite different from the red salt of α -benzildioxime. A similar colored compound is given by Hieber and Leutert (Ber., 62B, 1839 (1929)) which was obtained from γ -benzildioxime.

107. Edelman, L. E., "Preparation of New Compounds of Trivalent Nickel," J. Am. Chem. Soc., 72, 5765 (1950) [CA, 45, 4165d (1951)]7.

By treating either bromine or iodine with nickel α -benzildioxime suspended in carbon tetrachloride, complex nickel(III) salts were precipitated. The similar reaction with chlorine results in the formation of a purple solution which is unstable. Both the α -benzildioxime nickel(III) bromide and iodide are insoluble in water and all organic solvents except pyridine. Concentrated solutions of bases react to give a compound which decomposes slowly to α -benzildioxime.

1951

108. Pallaud, R., "Dioximes and Monoximes of the α -Diketones as Analytical Reagents," Chim. anal., 33, 239 (1951) [CA, 45, 8934g (1951)]7.

The properties and uses of the following oximes are described: dimethylglyoxime, α -benzildioxime, α -furildioxime, γ -benzildioxime, benzylmethylglyoxime, benzoylmethylglyoxime, phenylglyoxime, cyclohexanedionedioxime, diacetylmonoxime, oxalenediamidoxime, oxalenediuramidoxime, and isatine- β -oxime.

1952

109. Souhay, P., and Ser, S., "Polarography of Oximes," J. chim. phys., 49, C 172 (1952) [CA, 46, 5459e (1952)]7.

Polarograms were obtained in 10 or 20% alcoholic solutions containing 0.001 M benzildioxime and related compounds.

110. Weiss, A., and Hofmann, U., "Reactions Inside the Layer Lattice of Carnotite," Z. Naturforsch., 7b, 362 (1952) [CA, 47, 4166h (1953)]7.

A synthetic carnotite of the formula $[K(H_2O)_n][UO_2VO_4]$ and the cation exchange capacity of 220 meq./100 g. of air-dry powder exchanged its K^+ against Na^+ (I), Mg^{2+} (II), Ni^{2+} (III), arginine (IV), lysine (V), and aromatic amines. The magnesium ions in II can be precipitated inside the crystals with quinalizarin; the color changes thereby from light yellow to dark green. The nickel ions of III are precipitated and fixed with a methanol solution of dimethylglyoxime. In both cases hydrogen ions instead of the metal ions are exchangeable after the precipitation. α -Benzildioxime, however, is incapable of precipitating the nickel inside the layers.

111. Fujikawa, F., Tokuoka, A., Takimura, M., and Miura, K., "Antiseptics for Foods. LI.," J. Pharm. Soc. Japan, 72, 518 (1952); cf. F., Tokuoka, and Nakatani, Ibid., 71, 767 (1951) [CA, 46, 8779e (1952)].

This is a study on preservation of food by several oximes, acids, dioximes, etc. The extent to which α -benzildioxime acted as an antiseptic in preventing mold in soy sauce was almost identical as the antiseptic value of the control. At a concentration of 0.01%, mold was prevented for 77 days.

112. Banks, C. V., and Vander Haar, R. W., "Magnetic Studies of Nickel Complexes With Some vic-Dioximes," U. S. Atomic Energy Comm., ISC-250, (1952) [CA, 50, 9075h (1956)].

Magnetic susceptibilities of crystalline complexes of nickel(II) with α -benzildioxime and other related dioximes were studied by the Gouy method. These complexes are diamagnetic and thus presumably square coplanar in character. Magnetic and spectrophotometric studies showed that these complexes dissolved without change in chloroform or *o*-dichlorobenzene. In pyridine or *n*-butylamine more or less reaction occurs, depending on the complex, and a paramagnetic species is produced. There is a decrease in an absorption band at about 4000 Å. which is usually attributed to the diamagnetic square complex. α -Furildioxime and α -benzildioxime were the least and next least stable, respectively, toward reaction with pyridine or *n*-butylamine.

1953

113. Yamasaki, K., and Matsumoto, C., "Colors of Complex Nickel o-Dioximates," Sci. Repts. (Osaka Univ.), No. 2, 35 (1953) (in English) [CA, 49, 8724d (1955)]7.

Absorption curves are reported for nickel α -furildioximate (I), α -benzildioximate (II), and dimethylglyoximate (III) in solution in chloroform and in the colloidal state in water. Absorption maxima of I and II appear at 410 m μ and at 430 m μ , respectively, whereas no maximum appears on the curve of III. Colloidal suspensions of these compounds in water show quite different curves from the corresponding chloroform solution, with a characteristic absorption band in the visible region, which is attributable to the hydrogen bridge bond in the molecule. Absorption curves for water-soluble oxidized nickel dioximates and a discussion of these curves are also given.

114. Sone, K., "Absorption Spectra of Some Metallic Chelate Compounds," J. Am. Chem. Soc., 75, 5207 (1953); cf. Yamasaki, Yokoi, and S., J. Chem. Soc. Japan, Pure Chem. Sect., 69, 137 (1948) [CA, 48, 1808f (1954)]7.

The visible and ultraviolet absorption spectra of chloroform solutions of about 20 chelate compounds of cobalt, nickel, copper, palladium, and iron with 8-quinolinol, salicylaldehyde, salicylaldoxime, salicylaldimine, and dimethyl- and diphenylglyoxime are reported. The weak bands of the central metallic cation, the strong bands due to the ligand, anomalous bands due to a chromophore, and the correlation of stability of the complex and shift in absorption are discussed.

1955

115. Peshkova, V. M., "Effect of the Structure of the Oxime Molecule on the Properties of Its Compounds with Metals," Zhur. Anal. Khim., 10, 86 (1955); J. Anal.

Chem. U.S.S.R., 10, 77 (1955) (English Translation)

[CA, 49, 15594h (1955)]

The nature of a dioxime determines the pH range at which it precipitates metals, primarily nickel. As the length of the alkyl chain increases, the pH at which nickel is precipitated is lowered. The benzene ring has a similar effect; α -benzildioxime precipitates nickel at pH 4.2-11. The most stable nickel precipitate is formed by the dioxime of 1,2-cyclohexanedione. The molecular weight of the dioxime and its solubility in water do not greatly affect the properties of the nickel precipitate. The molecular structure of dioximes also affects their suitability for colorimetric determination of their metal complexes. A number of dioximes were studied for their molar coefficients of extinction and their coefficients of distribution between an aqueous and nonaqueous medium (extractant).

116. Banks, C. V., Vander Haar, R. W., and Vander Wal, R. P.,

"Magnetic Studies of Nickel(II) and Palladium(II)

Complexes with Some vic-Dioximes," J. Am. Chem. Soc.,

77, 324 (1955) [CA, 49, 5905e (1955)]

Complexes of the following dioximes with nickel(II) were studied magnetically: α -benzildioxime, α -furildioxime, 2,3-butanedionedioxime, and 1,2-cyclohexanedionedioxime. The corresponding palladium(II) complexes were also studied, except for the last-mentioned oxime. At 20° the molar susceptibilities ($\times 10^6$) ranged from -108 to -296, the data being precise and accurate to within 2-3%. All the complexes are diamagnetic, and presumably have square coplanar structures, similar to that for nickel 2,3-butanedionedioxime (Godycki and Rundle, Acta Cryst., 6, 487 (1953)).

117. Yamasaki, K., and Matsumoto, C., "o-Diketone Dioximes and

Their Metallic Complexes. I. Benzil Dioxime and Its

Nickel and Palladium Complexes," J. Chem. Soc. Japan,

Pure Chem. Sect., 76, 569 (1955) [CA, 50, 11156g

(1956)]

Anti (α) and amphi (γ) forms of the oxime both gave complexes of the compositions $M(\text{oxime})$ and $M(\text{oxime})_2$. Colors of the complexes of the anti form were brighter than those of the amphi form.

118. Yamasaki, K., and Matsumoto, C., "o-Diketone Dioximes and Their Metallic Complexes. II. Color of Nickel Dioximate," J. Chem. Soc. Japan, Pure Chem. Sect., 76, 736 (1955); cf. Y. and M., Sci. Rpts. (Osaka Univ.), No. 2, 35 (1953); Y. and M., J. Chem. Soc. Japan, Pure Chem. Sect., 76, 569 (1955) [CA, 50, 13643a (1956)].

Nickel complexes of dimethylglyoxime, benzildioxime, and furildioxime are yellow in chloroform solution and red as solids. They are monomeric in solution and polymeric in the solid state. Addition of bromine and dimethylglyoxime to the ammoniacal solution of nickel gives a red solution, which has two bands, at 450-460 and 540-570 m μ , and can be used for the determination of nickel.

119. Boyer, J. H., Reinisch, R. F., Danzig, M. J., Stoner, G. A., and Sahhar, F., "The Transformation of ψ -o-Dinitroso Aromatic Compounds into o-Nitroaryl Amines," J. Am. Chem. Soc., 77, 5688 (1955) [CA, 50, 8493e (1956)].

Benzil (50 g.) and 50 g. hydroxylamine hydrochloride in 400 cc. methanol refluxed for three hours, the solution cooled, filtered, and the residue recrystallized twice from methanol yielded 34 g. α -benzildioxime (m.p. 238-40°). The combined mother liquors diluted with water gave 25% β -isomer (m.p. 205-6°). α -Benzildioxime (15 g.) in 100 cc. 10% sodium hydroxide, diluted with 200 cc. water, treated with 350 cc. 1.000 N sodium hypochlorite, filtered, washed, dried, and recrystallized gave diphenylfuroxan (m.p. 118°).

1956

120. Uzumasa, Y., and Washizuka, S., "Ultraviolet Spectrophotometric Determination of Nickel with α -Benzildioxime," Bull. Chem. Soc. Japan, 29, 403 (1956) (in English); cf. Atack, Chemiker-Ztg., 37, 773 (1913) CA, 50, 12741e (1956) 7.

A new method is described for the extraction of nickel(II)-benzildioxime with chloroform and the spectrophotometric measurements of the colored system in the same solvent. The wide pH range for the extraction eliminates the use of a buffer, and nickel is readily separated from iron(III), aluminum, zinc, chromate, vanadate, and molybdate. By obviating the excessive benzildioxime with dilute alkali, sensitive absorption readings are achieved, and the sensitivity at 275 m μ is 0.0013. Beer's law holds up to 1 p.p.m. of nickel at 275 m μ , and up to 4 p.p.m. at 358 and 406 m μ . The nature and degree of interference of copper and cobalt on the color development are discussed also, and their allowable amounts were determined. About 15 ml. of slightly acidic sample solution containing up to 20 γ of nickel were placed in a glass-stoppered test tube and 2 or more ml. 10% sodium tartrate or citrate solution were added to prevent the precipitation of iron(III) hydroxide. The solution was then made ammoniacal, 2 ml. of 0.02% α -benzildioxime solution added, the test tube shaken as the red precipitate appeared, 5 ml. chloroform added, the contents shaken, and precipitate extracted. The aqueous layer was removed by suction, 10 ml. 1% sodium hydroxide solution introduced into the tube, the alkaline layer removed by suction, and the chloroform layer washed once with 10 ml. 0.5% ammonium hydroxide, and then with two 10-ml. portions of 1% sodium hydroxide solution. After the last washing the liquid was almost completely removed, the chloroform solution was taken up with a pipet and filtered into the quartz cell for comparison with standard nickel solutions, which had been prepared by the same procedure. The allowable concentration for copper is as high as 0.1 mg. and for cobalt 0.01 mg. when as much as 5 γ of nickel is to be determined. Copper is readily extracted into the chloroform phase from which it is eliminated by washing with sodium hydroxide solution and ammonium hydroxide. In case its concentration is higher than 0.1 mg., however, copper may hinder nickel from reacting with the reagent, and the amounts of the reagent as well as chloroform must be increased.